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Inhibition efficiency of synthesized petroleum sulfonates mixtures against the acidic corrosion of mild steel

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Abstract

The inhibiting effects of surfactants synthesized by sulfonation from Algerian petroleum products (crude oil, gasoil, kerosene and platformat) of local origin (field of Hassi Messaoud in the south of Algeria) against the acidic corrosion of mild steel were determined by electrochemical techniques: polarization resistance (RP), polarization curves (Tafel slopes) and electrochemical impedance spectroscopy (EIS). The results showed that the inhibition effectiveness is a function of the nature and the families' contents of hydrocarbons in the initial products on one hand and of the physicochemical properties such as: solubility and critical micelle concentration (cmc) on other hand. It increases in the direction: platformat, kerosene, gasoil and crude oil. The examination of the isotherms showed that adsorption verifies the model of Temkin for the crude oil surfactant and the model of Frumkin in the other cases. The rise of temperature, in the field 30-60°C, decreases the effectiveness which indicates a physisorption of surfactants at steel surface, however it remains relatively significant compared with inhibitors of same type.

Keywords: mild steel corrosion, inhibiting effect, surfactant, oil sulphonates, hydrocarbons

1. Introduction

The protection of oil and gas structures against corrosion consumes large amounts of inhibiting substances in order to preserve their integrity for long duration [1-2]. The effectiveness, reliability and the cost are the most decisive criteria in the choice of these substances. The inhibiting effects of surfactants synthesized from petroleum products, against corrosion of different metals in aggressive media, were the subject of many studies [3-7]. It was shown that the effectiveness of synthesized compounds depends on the origin, the nature and the specific characteristics of the basic petroleum products (aromatic, naphthenic and paraffinic contents) [5, 8]. The reaction of synthesis generates active centers which are able to improve its adsorption on the surface of metal. These active centers should contain at least one donor atom such as nitrogen, sulphur, phosphorus, and/or oxygen, which exchange "coordinate bonds" with metal [9, 10]. This study had as objective firstly to synthesize surfactants by sulfonation of some hydrocarbons (gasoil, platformat, kerosene and the crude oil) of local origin (field of Hassi Messaoud in the south of Algeria), secondly to evaluate their inhibition effectiveness against the corrosion of mild steel in aggressive media by electrochemical techniques. The correlation between the inhibiting effect and some characteristic parameters: critical micelle concentration (cmc), solubility, and families contents of hydrocarbons were examined.

2. Materials and methods

2.1. Petroleum products

Petroleum products used are: kerosene (KN), gasoil (GO), plat format (PF) and crude oil (PB), provided by the refinery of Algiers. Oil cuts (kerosene, gasoil and platformat) were obtained by atmospheric distillation of crude oil. Contents in hydrocarbon families: aromatic X_{ar}, naphthenic X_{np} et paraffinic X_{pf} , evaluated by ndPa method [8].

Table 1: Contents of petroleum products as percentage of hydrocarbons families.

(%)	Platformat (PF)	Kerosene (KN)	Gasoil (GO)	Crude oil (PB)
X_{ar}	42.03	14.02	7.66	6.33
X_{np}	11.36	23.68	28.44	25.39
X_{pf}	46.61	62.30	63.9	68.28

2.2. Sulfonation

The sulfonation reaction was carried out according to [5, 11]. The experimental set-up includes Pyrex tricol balloon of 1L, addition ampoule, line of degasification and thermometer. The unit bathes in thermostatically-controlled bath. The reagents are from Merck or Fluka. The surfactants obtained after sulfonation are: sulfonates of Gasoil (SGO), of Plat format (SPF), of crude oil (SPB) and of Kerosene (SKN).

2.3. Characterization of synthesized surfactants

2.3.1. Determination of critical micelle concentration (cmc) and solubility

The critical micelle concentration (cmc) was determined by conductimetry in 3% NaCl solution according to [9]. A conductimeter EC214-215 HANNA was employed.

The solubility was determined by agitating saturated solutions during 15 min at least, and then it is left at rest at the ambient temperature. After equilibrium, the aqueous phase is analyzed by UV spectroscopy.

2.4. Inhibition efficiency determination

2.4.1. Electrochemical Cell

The mild steel X60 used had the following chemical composition (wt.%) : C, 0.176 ; Mn, 1.500 ; Si, 0.320 ; S, 0.043 ; Cu, 0.042 ; Nb, 0.018 ; Cr, 0.012 ; P, 0.01 ; Ni, <0.02; Fe, balance. The working electrode, in the form of a disc cut, has a geometric area of 0,78 cm^2. A 300 ml-capacity three-electrode cell, thermostatically-controlled was used. A saturated calomel electrode (SCE, +0.24 V/ESH) and platinum mesh electrode (4x4 cm^2) are respectively used as reference and auxiliary electrode. Solutions of NaCl, 3% (in wt.) at pH 3, were prepared with distilled water and deaerated by argon for 30 min prior to each insertion of electrode.

2.4.2. Electrochemical Measurements

The inhibiting effect was determined by: polarization resistance (RP), polarization curves (Tafel slopes) and electrochemical impedance spectroscopy (EIS).

Electrochemical experiments were carried out by means of EG&G Instruments electronic equipment. It includes Potentiostat/Galvanostat (PAR 273A) and a 5210 Two Phase Lock-in Analyzer. EIS measurements were carried out at the open circuit potential (OCP).

2.4.3. Calculation of the inhibition efficiency

The inhibition efficiency can be calculated on the basis of the data from the electrochemical experiments by:

$$\boldsymbol{E\% = \left(1 - \frac{x}{x_o}\right).100} \qquad (1)$$

where x_O and x are either the corrosion rate (from weight loss measurements), or the corrosion current density (from polarization curves) in the absence and in the presence of inhibitor respectively, or otherwise the charge transfer resistance (EIS) in the presence and in absence of the inhibitor, respectively.

3. Results and discussion

3.1. Inhibition efficiency (E%)

3.1.1 Effect of the inhibitor concentration at 30°C

Figure 1 presents the dependence of the inhibition efficiency E(%) on the concentration (mg/L). Firstly, results from all techniques are in good agreement. Secondly, for each surfactant, E% increases with the concentration of the inhibitor until an optimal value (efficient concentration) after which it decreases up to relatively low values. By adsorbing on the metal surface, inhibitors control the anodic and/or cathodic reactions during corrosion process, and the inhibition efficiency is proportional to the amount of inhibitor adsorbed. During the adsorption process, the functional group and the structure of the inhibitor molecule have important roles.

Electrostatic attraction between the charged hydrophilic groups and the charge active centres on the metal surface leads to physisorption. Several authors showed that most organic inhibitors are adsorbed on the metal surface by displacing water molecules from the surface and forming a compact barrier film. It was assumed [12-13] that the mechanism of the corrosion process of steel in corrosive solution with added inhibitor can be described as following:

$$\mathbf{Fe} + \mathbf{inh}_{sol} \rightleftharpoons \mathbf{Fe(Inh)_{ads}} \rightleftharpoons \mathbf{Fe^{n+}} + \mathbf{ne^-} + \mathbf{inh}_{sol} \qquad (2)$$

In the beginning, there is formation of Fe(Inh)ads to cover the metal surface. E% increases with the inhibitor concentration. At the same time, metal dissolution takes place on free steel surface sites. With higher inhibitor concentration and especially nearby or above cmc, the maximum of E% is reached. Compact inhibitor overlayer is formed which reduces chemical metal attacks. Beyond this value, the inhibiting effect decreases with the increasing of the concentration. This latter phenomenon can likely be ascribed to special interactions resulting from mecellar exclusion or precipitation.

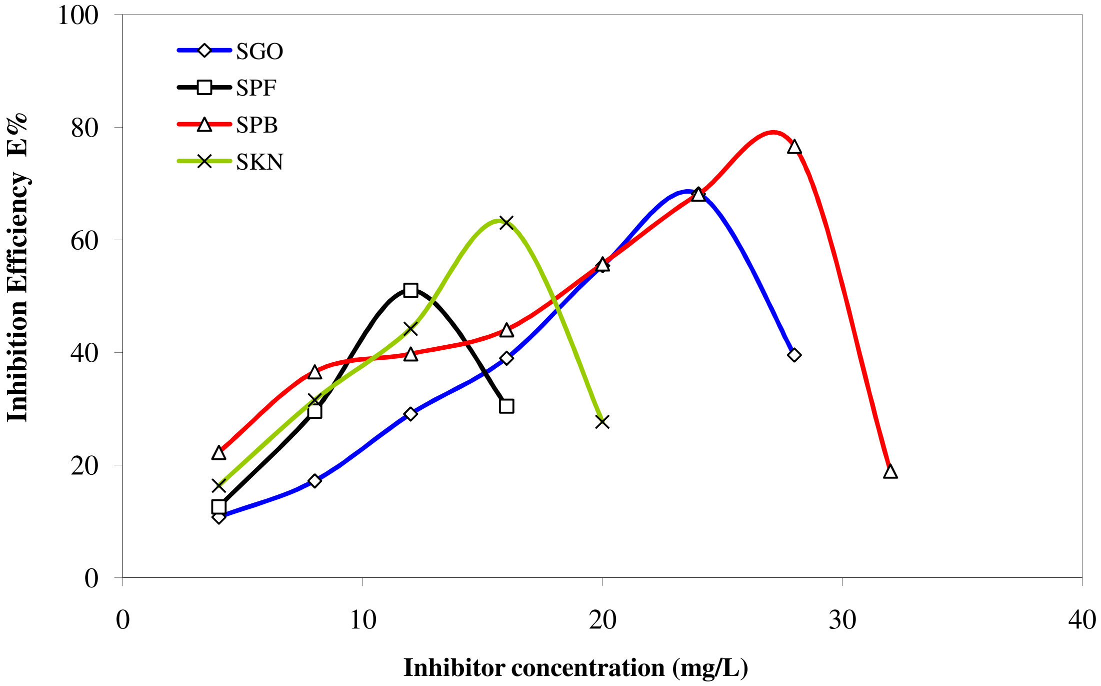

Figure 1: Inhibition efficiency (E%), determined by EIS, as function of concentration.

3.1.2 Effect of the composition of the petroleum product

By analyzing the results of the 4 inhibitors, table 1 and 2, it appears obvious that the inhibition effectiveness is a function of the nature and the contents of hydrocarbons families (aromatic, naphthenic and paraffinic) in the original products. More the content of paraffinic and naphthenic is high even more the effectiveness is better. The effect of paraffinic percentage is more pronounced. According to the maximum inhibition efficiency, the inhibitors are ranked as follows:

SPF (51%) < SKN (63%) < SGO (68.1%) < SPB (76.6%).

3.1.3 Dependence of the inhibition efficiency on cmc, and solubility.

The surfactants solutions are characterized by critical micelle concentration (cmc), where surfactants change their initial molecular solvated state and most of the physicochemical properties of solutions undergo an abrupt variation at this concentration [14]. The data, Table 2, show clearly that, in all cases, the inhibition efficiency increases when the concentration of the surfactant increases and tends to attain maximum. The higher inhibition efficiency was observed when the concentration of surfactant reached or exceeded its cmc.

Table 2: Solubility, critical micelle concentration (cmc), efficient concentration and maximum inhibition efficiency.

	Solubility, mg/L	cmc, mg/L	Efficient conc., mg/L	E%
SPF	42.0	12.0	12.0	51.04
SKN	90.0	15.0	16.0	63.03
SGO	95.0	20.0	24.0	68.14
SPB	130.0	22.0	28.0	76.6

According to [15], the inhibition efficiency scarcely changes when the surfactant concentration exceeds the critical micelle concentration (cmc); it tends rather to decrease. Indeed, when a maximum is observed, it is likely due to the change in surfactant monomer concentration, micellar exclusion or precipitation [9]. In addition, we show that as well as the efficient concentration and the cmc vary with the nature of the surfactant, solubility also changes. The solubility increase is accompanied obviously by an increase of the inhibition performances.

3.3. Adsorption isotherms

Adsorption of organic compounds can be described by two main types of interactions: physisorption and chemisorption processes, which are influenced by the nature and charge of the metal, the chemical structure of the inhibitor and the type of electrolyte.

It is assumed that E%, calculated from Eq. (1) is comparable to the degree of coverage of metal surface by an inhibitor, (θ) [16]. The best fit was obtained by assuming the Frumkin isotherm in the form given by Eq.3 for SPF, SKN and SGO; and Temkin isotherm in the form given the Eq.4 for SPB [17].

$$\textbf{Frumkin isotherm:} \quad \frac{\theta}{C(1-\theta)} = \mathbf{K.\exp(2a.\theta)} \qquad (3)$$

$$\textbf{Temkin isotherm:} \quad \mathbf{KC = \exp(-2a.\theta)} \qquad (4)$$

In these two equations C is the concentration of inhibitor. Further, K is the adsorption equilibrium constant related to the free energy of adsorption ΔG_{ads} by:

$$\mathbf{K} = \frac{\mathbf{1}}{\mathbf{C_{solvent}}}.\mathbf{\exp} -\left(\frac{\mathbf{\Delta G_{ads}}}{\mathbf{RT}}\right) \qquad (5)$$

Where $C_{solvent}$ is the molar concentration of solvent, R the ideal gas constant, T the absolute temperature.

Table 3: Free adsorption enthalpy ΔG_{ads} of different inhibitors.

	SPF	**SKN**	**SGO**	**SPB**
ΔG°_{ads} (kJ.mol^{-1})	-32.90	-33.63	-32.59	-40.43

ΔG_{ads} values calculated are negative in accordance with Eq. (5) suggesting the spontaneity of the adsorption process.

The calculated values of free energy of adsorption ΔG_{ads}, table 3, seem to suggest a physical adsorption and a slight part of chemical adsorption [18-22]. On the other hand, the values of the free energy of adsorption were much lower, around –33 kJ.mol^{-1} for SPF, SKN and SGO. Whereas, SPB, which had the more important inhibition effect, is characterized by a more negative value of ΔG_{ads}. This indicates that SPB shows stronger adsorption strength and chemisorption is more adequate [23-25].

3.4. Effect of temperature and activation energy

Temperature has a great effect on the rate of metal electrochemical corrosion. In case of acid medium, the corrosion rate increases exponentially with temperature because the hydrogen evolution overpotential decreases. An experimental dependence of Arrhenius type is observed between the corrosion rate and temperature [26,27]:

$$i_{corr} = \mathbf{k} . \mathbf{exp} -(\frac{\mathbf{E_a}}{\mathbf{RT}}) \qquad (6)$$

where E_a is the effective activation energy of the corrosion process, R the ideal gas constant, T the absolute temperature, k the Arrhenius pre-exponential factor and i_{corr} the corrosion current density. It provides the determination of the effective activation energy of the corrosion process.

The effect of surfactants synthesized on the corrosion process at four different temperatures has been studied, table 4. The inhibition efficiency and the activation energy (E_a) have been estimated in the presence and in the absence of 12 mg/L of the inhibitors.

Table 4: Temperature dependence of the inhibition efficiency with the presence of 12 mg/L of surfactant.

Temperature K	Inhibition Efficiency E%			
	SGO	SPF	SPB	SKN
30	29.37	51.15	41.62	44.82
40	25.96	31.50	10.14	13.25
50	22.46	33.31	11.90	12.95
60	18.99	26.50	11.75	11.16

The values of E_a for the five samples obtained from the slope of the lines are given in Table 5. The data shows that the values of E_a are higher than those in the uninhibited acid solution. This thermodynamic function enhances in general with increasing the inhibitor concentration, indicating that more energy barrier for the reaction in the presence of the inhibitor is attained. Temperature increase leads to a decrease in E%, with the resulting variation of the effective activation energy value, which is higher than that in the absence of the inhibitor as shown in table 5. This can be owing to the decrease in the strength of adsorption process at higher temperatures, suggesting a physical adsorption of inhibitors on the surfaces [5-7,28-30].

Table 5: The apparent activation energy (E_a) calculated in the absence and in the presence of 12 mg/L of the inhibitors.

	blank	SGO	SPF	SPB	SKN
E_a (kJ.mol^{-1})	27.22	31.06	37.39	37.69	39.44

Conclusion

The inhibition efficiencies determined by the three electrochemical methods are in good agreement. The results obtained indicate that, the four surfactants synthesized have good inhibiting effects on the corrosion of mild steel in NaCl (wt.3%, pH=3). According to the maximum inhibition efficiency, the inhibitors are ranked as follows: SPF(51.0%) < SKN(63.0%) < SGO (68.1%) < SPB(76.6%). The effectiveness is better when the content, of paraffinic and naphthenic, is higher. The shape of the adsorption isotherms, confirm the applicability of Frumkin's equation to describe the adsorption process of the three surfactants: SPF, SKN, SGO and Temkin's equation to the surfactant SPB.

The higher inhibition efficiency is observed when the inhibitor concentration reaches values close to, or exceeds the cmc. Beyond this value, the inhibiting effect decreases with the increasing of the concentration.

The inhibition efficiency decreases with the temperature rise. The process of the inhibition is likely due to the formation of a physically adsorbed film on the metal surface.

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