CORROSION PROTECTION OF CARBON STEEL IN SEAWATER BY ALUMINA NANOPARTICLES WITH POLY(ACRYLIC ACID) AS CHARGING AGENT

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Nanostructured Al_2O_3 in 60-80 nm diameter has been deposited on carbon steel substrates, by cathodic electrophoretic deposition (EPD), in ethanol with poly(acrylic acid) (PAA) as charging agent, as a protective coating against corrosion for carbon steel (C.S.) in seawater environment. Potentiodynamic polarization measurements performed on the Al_2O_3 coated carbon steel coated by Al_2O_3 in 3.5 % NaCl at temperature range 298-328 K and the result showed that using PAA charging agent lead to increase the corrosion resistance.

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Introduction

Corrosion is a natural phenomenon and is accompanied by the flow of electrical current involving the reversion from metallic to compound state. So it becomes clear that corrosion cannot be fully prevented instead it can be controlled to a greater extent. Many researchers have used various methods in corrosion prevention investigations, such as coated metal surfaces by nanoparticles.

The use of particles in nano scale could also change the microstructure of the electrodeposits leading to a more compact structure and thus to improved corrosion resistance.[1,2] Nanoparticle coatings possess good thermal and electrical properties and they are resistant to oxidation, corrosion, erosion and wear in high temperature environments.[3] These properties are very important factors in the applications such as pipelines, castings and automotive industry.

Electrophoretic deposition (EPD) is one of the liquid coating methods,[4–6] which elaborates stable suspensions of Al_2O_3 particles in an appropriate liquid. Both sparse Al_2O_3 particles and dense particle coating layers on metal surface have been invented. Generally, EPD consists of two processes, i.e. the movement of charged particles in suspension in an electric field between two electrodes and the particle deposition on one of the electrodes to be protected. The mechanism of the formation of a deposit during EPD is reviewed and discussed in several theoretical papers and reviews.[7-9]

The insufficiency of surface charge and excessive weight potentially can be overcome through the use of polymeric charging agents, EPD with ethanol as suspension medium and poly(acrylic acid) (PAA) as polymeric charging agent give good protection. Further, these polymeric charging agents play an important role as binders to improve adhesion between deposited particles and substrate.[9,10]

The aim of the present work was to examine the efficiency of Al_2O_3 nanoparticles (NPs) to protection of carbon steel (C.S.) using absolute ethanol as suspension medium and a PAA polymeric charging agent.

Experimental

Materials

The steel used in this study is a carbon steel (C45) with a chemical composition (in wt %) of 0.42 % C, 0.40 % Si, 0.50 % Mn, 0.045 % S, 0.40 % Cr, 0.045 % P, 0.40 % Ni, 0.0.1 % Mo and the remainder is iron (Fe).The carbon steel samples were pre-treated prior to the experiments by grinding with emery paper SiC (120, 600 and 1200); rinse with distilled water, degreased in acetone, washed again with distilled water and then dried at room temperature before used synthesized seawater. The seawater solution was prepared by dissolved 35 g NaCl in 1L distilled water. Al_2O_3 Nanoparticles were used in diameter range (20-30nm, Hongwu nanometer, purity 99.9%) and iodine was used in 99.8% purity (Aldrich).

Preparation of emulsion solution

Emulsion solution was prepared by adding 1 % Al_2O_3 NPs powder to ethanol as solvent [16] (adding 1.5 g NPs to 150 mL ethanol). To study the effect of adding different percentages of PAA (0.1, 0.25, 0.5 and 1%) in emulsion solution (0.1, 0.25, 0.5 and 1g) of PAA was added to 100 mL ethanol respectively.

To homogenize the solution, an ultrasonic (50 W) stirrer was used to mixed the solution for 30 min. The solutions were applied for coating C.S. pieces by using EPD technique method. Sometime few iodine crystals were added to increase conductivity.[11]

Electrophoresis deposition of emulsion solution (coating samples)

To deposit emulsion solution on a piece of C.S.. surfaces, deposition cell device was used. The electrodes were connected to a D.C power supply, it can be used in anodic or cathodic deposition by reversing electrodes of the power supply.[12] The deposition cell device composed of the following components: A beaker of 250 mL capacity and the cover contains two slit with distance between then equal to 1 cm. Power supply used to supply constant direct current D.C voltage was varied between 0 and 20 V. An electrical circuit was connected by ammeter, respectively, to measure the current generated between the poles. Stainless steel rode used as inert electrode in deposition process cell.[13] A piece of carbon steel catch by tong made of stainless steel fixed with 1cm distance between it and inert electrode.

The deposition on C.S. specimens were carried for 3, 4, 5 and 6 minutes, then all specimens thermally dried at 150 °C for 2 min.

Electrochemical measurements

The electrochemical measurements were carried out using Mlab (Germany, 2000) potentiostate and controlled by a computer and MLabSci software which were used for data acquisition and analysis under static condition. The corrosion cell used had three electrodes, the reference electrode was a silver- silver chloride, platinum electrode was used as auxiliary electrode with 1 cm^2 surface area and the working electrode was carbon steel. All potentials given in this study were referred to this reference electrode. The working electrode was immersed in test solution for 15 min to a establish steady state open circuit potential (E_{ocp}), then electrochemical measurements were performed in potential range (±200) mV. All electrochemical tests have been performed in aerated solutions at 208-328 K.

Results and discussion

Effect of time

The deposition on C.S. specimens were carried for (3, 4, 5 and 6) minutes, to study the effect of time on the deposition on C.S. specimens and chose the optimization time for deposition to get high protection efficiency. The perfect time for coated C.S. by Al₂O₃ NPs using EPD technique was 6 min, which gave percentage of protection efficiency (PE %) as 83.9 % at 298 K as shown in Figure 1.

Polarization curve

Figure 2 shows the polarization curves for the corrosion of carbon steel coated with Al₂O₃ NPs in absence and presence of various amounts of PAA. It could be observed that both the cathodic and anodic reactions were suppressed with the addition of different amounts of PAA, which suggests that coating by Al₂O₃ in the absence PAA lead the polarization curve shifting to more positive value (less active) reach to -730.0 mV at 328 K but when PAA was added in different

concentration, the value of corrosion potential shifted to more active value but don't reach to the corrosion potentials of uncoated C.S.
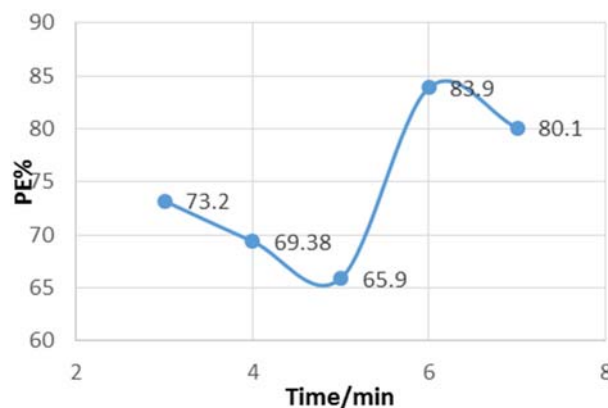

Figure 1. Relationship between PE% and coating time for coated C.S. by Al₂O₃ NPs at 298K.

PE % of all types of coating estimated by comparison with the measurements of the uncoated surface of carbon steel alloy using Eqn. (1).

$$PE\ \% = \frac{(i_{\text{corr uncoated}}) - (i_{\text{corr coated}})}{(i_{\text{corr uncoated}})} \times 100 \tag{1}$$

where $i_{\text{corr uncoated}}$ and $i_{\text{corr coated}}$ are corrosion current densities for uncoated and coated specimen, respectively.
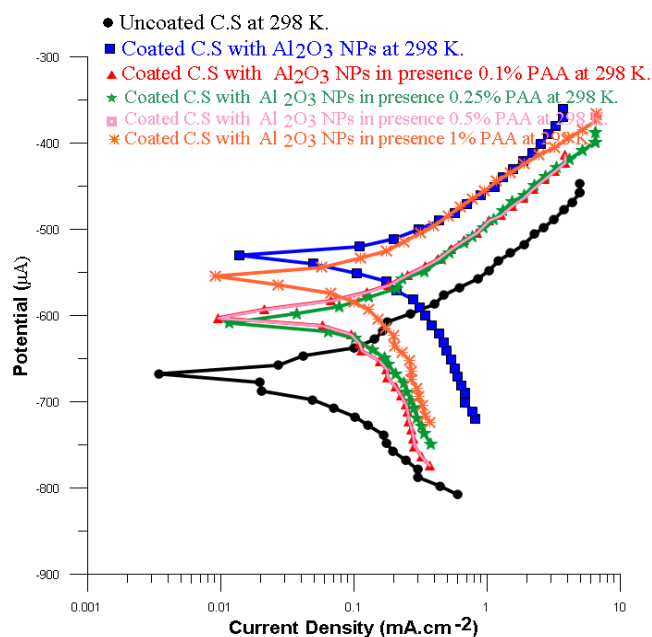

Figure 2. Polarization curves for C.S. in 3.5 % NaCl for uncoated and coated C.S. with Al₂O₃ NPs in absence and presence of PAA.

Effect of PAA

The thickness of coat layer on C.S. surface can be measured using eqn. (2)

$$\rho = \frac{Wt}{V}$$

(2)

where ρ is the density of NPs, Wt is weight of the coat and V is volume of the coat.

$$V = r^2 \times 3.14 \times d$$

(3)

where r is the radius of C.S. piece and d is thickness of the coat.

The effect of adding different PAA concentration in the Al$_2$O$_3$ NPs suspension solution, were investigated. PAA lead to decrease the thickness of Al$_2$O$_3$ layers from 14.424 μm in the absence PAA to thickness ranging between 11.1 and 11.8 μm in presence of different concentration of PAA, as shown in Figure 3.
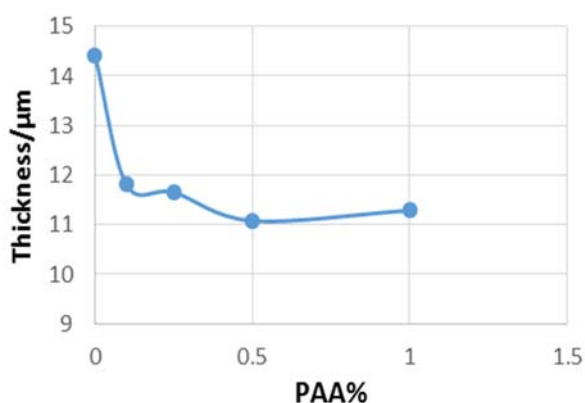
Adding 0.5 % of PAA for the suspension of Al$_2$O$_3$ coating lead to the lowest i_{corr} value in temperature range of 298- 328 K, as shown in Figure 4. So the best PE % was obtained in presence of 0.5 % PAA at 298 K. So 0.5 % PAA is the right concentration for addition to suspension solution of coating which give PE % ranging between 87–85 % in the temperatures range of 298- 328 K, as shown in Figure 5.

Figure 5. Effect of adding different PAA % to Al$_2$O$_3$ NPs coating suspension on PE %.

Surface Morphology

The morphologic analysis by AFM for layers of Al$_2$O$_3$ NPs without PAA and for Al$_2$O$_3$ NPs with 0.5 % PAA was done.

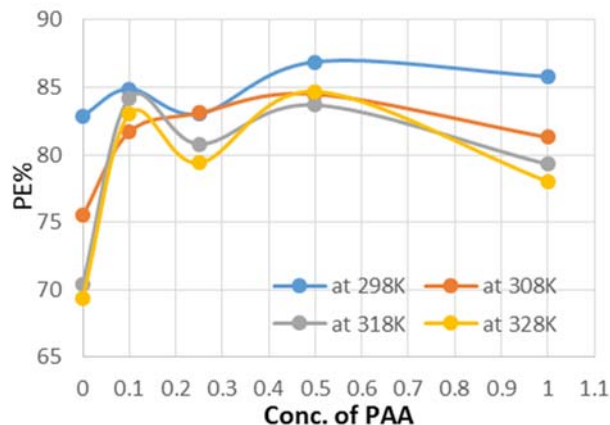**Figure 3.** Relation between thickness and PPA % after 6 min coating time with Al$_2$O$_3$.
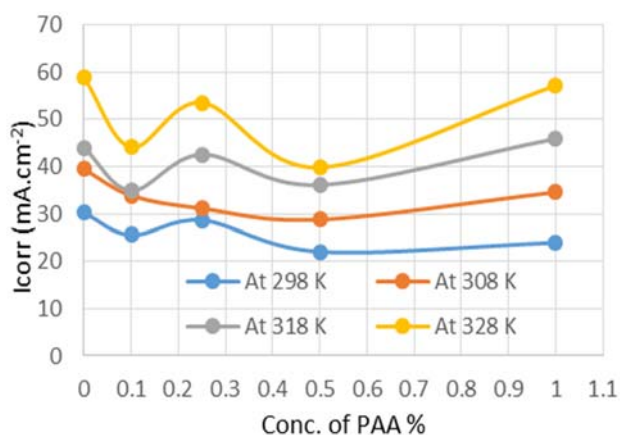
Figure 4. Effect of adding different PAA % to Al$_2$O$_3$ NPs coating suspension on i_{corr}.
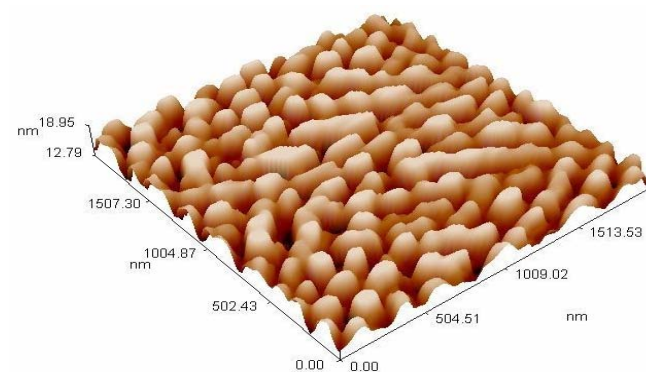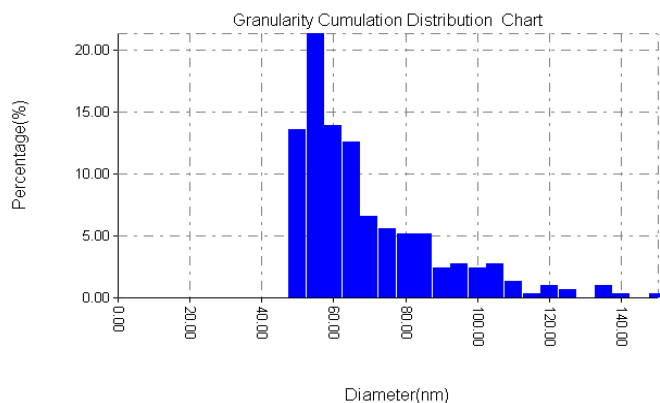
Figure 6. Granularity Cumulation Distribution and 3D views of AFM image of Al$_2$O$_3$ without PAA applied on carbon steel.
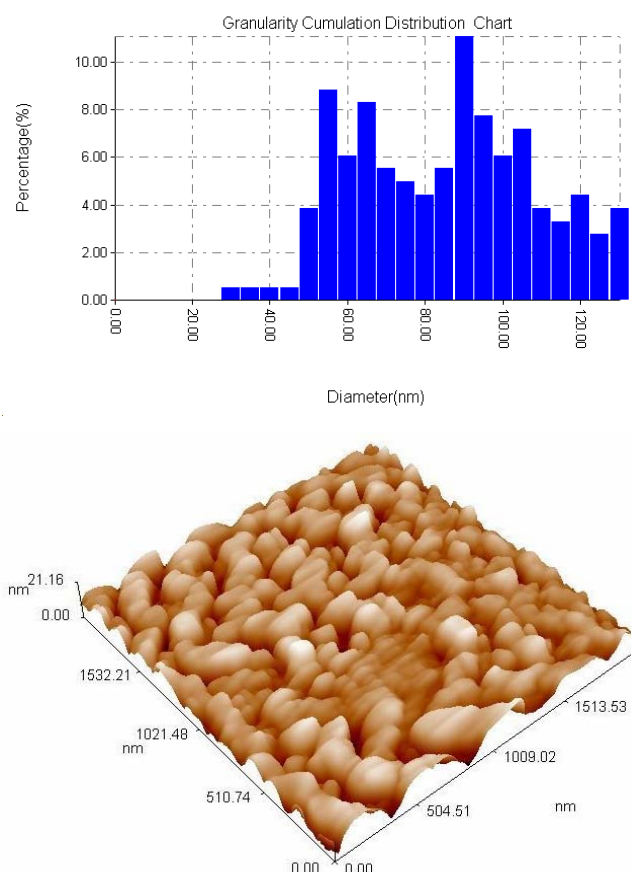
Figure 7. Granularity Cumulation Distribution and 3D views of AFM image of Al₂O₃ with PAA applied on carbon steel.

Since we started with alumina particles of 20-30 nm in diameter, AFM images shows little largest average particles sizes for the Al₂O₃ NPs without PAA and Al₂O₃ NPs with 0.5 % PAA, as shown Figures 6 and 7 respectively, and it reached around 66 nm and 82 nm respectively.

FT-IR Spectroscopy

Fourier transformation infrared spectra for Al₂O₃ NPs deposition on C.S. in presence PAA and the pure PAA show a multi peak band at 3304-3350 cm⁻¹ which indicates the presence of the OH group or N-H, which was not shown in the spectrum of pure PAA, also it shows a peak at 1735-1793 cm⁻¹ due to the presence of the carbonyl group for ketone. In this spectrum, there are bands at 1176 and 1172 cm⁻¹ indicating the presence of C=H groups.

Table 1. Wave number of FT-IR adsorption for pure PAA. and PAA/Al₂O₃ coat in C.S..

Pure PAA	Al₂O₃ NPs deposition in presence PAA	
Wave number, cm⁻¹	Wave number (cm⁻¹)	Assignment
-	3401,13	OH stretch
3143	3350	OH strech
1436	1458	C-O stretch
1176	1172	C=N stretch
1735	1739	C=O strech

Surface porosity

Surface porosity percentage fraction was estimated by potentiostatic polarization. In this case, the porosity percentage (*P* %) can be calculated using the following equation:

$$P\% = \frac{R_{\mathrm{p,uncoated}}}{R_{\mathrm{p,coated}}} 10^{-\left(\frac{\Delta E_{\mathrm{corr}}}{\beta_a}\right)} x\ 10 \tag{4}$$

where $R_{\mathrm{P,ucoated}}$ and $R_{\mathrm{P,coated}}$ are the polarization resistances of the uncoated C.S. and the coating C.S. by NPs, respectively, ΔE_{corr} is the corrosion potential difference between them, and β_a is the anodic Tafel coefficient of the uncoated C.S..

In general, adding PAA increase surface porosity percentage (P %) for coated C.S. by Al₂O₃ NPs at all concentration of PAA, 1 % PAA lead to higher P% which reach to 32.5 % at 328 K, as shown in Figure 8.
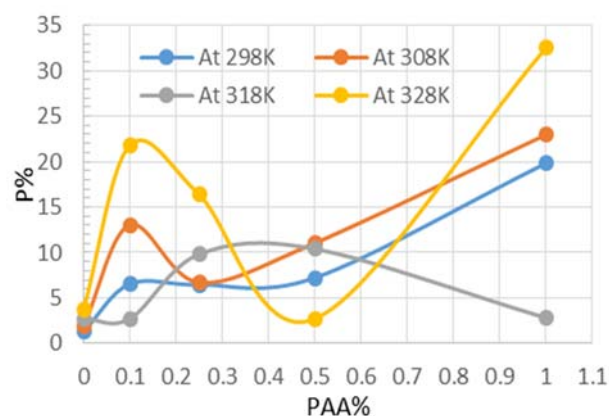

Figure 8. Variation of porosity percentage P% with PAA % at different temperatures.

Kinetic studies

The corrosion reaction can be regarded as an Arrhenius modified Arrhenius equation.[17]

$$\log i_{\mathrm{corr}} = \log A - E_a/2.303RT \tag{5}$$

where i_{corr} is the corrosion current density, E_a is the apparent activation energy of the corrosion reaction, R is the gas constant, T is the absolute temperature and A is the Arrhenius pre-exponential factor. Figure 9 presents the Arrhenius plots of the natural logarithm of the current density vs. $1/T$, for C.S. samples uncoated and coated C.S. by Al₂O₃ in presence and absence of different concentrations of PAA, in artificial seawater.

Values E_a and A for the corrosion reaction in the absence and presence of different concentrations of the PAA are calculated by a linear regression method and given in Table 2.
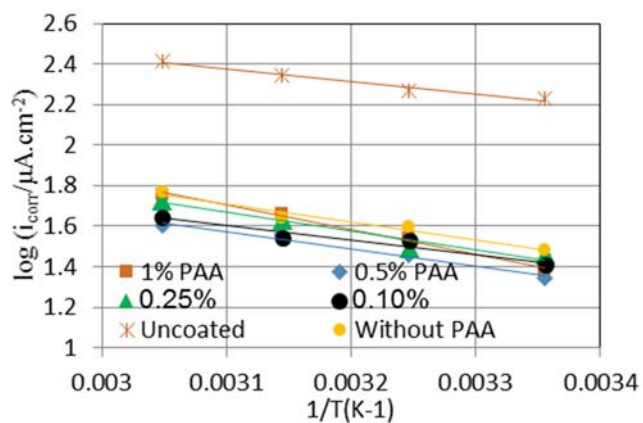
Figure 9. $\log i_{corr}$ vs $1/T$ for coated C.S. with Al$_2$O$_3$ NPs in absence and presence of different PAA % in 3.5 % NaCl.

It is found that the activation energy is increased after coating C.S. by Al$_2$O$_3$ in absence and presence PAA, and a higher value was obtained when C.S. coated with Al$_2$O$_3$ in presence 1 % PAA which reach to 23.54 kJ mol^{-1}. But Value of A increase slightly when C.S. is coated.

Table 2. Kinetic parametera for C.S. coated with Al$_2$O$_3$ in absence and presence of different PAA % in 3.5 % NaCl.

	Conc.	E_a kJ mol$^-$	A Molecules cm^{-2} s^{-1}
Coated by Al$_2$O$_3$	Uncoated	12.33	1.32 x 10^{28}
	Without PAA	20.10	3.271 x 10^{28}
	(0.1%) PAA	12.33	3.79 x 10^{28}
	(0.25%) PAA	17.69	2.02 x 10^{28}
	(0.5%) PAA	16.30	9.9 x 10^{27}
	(1%) PAA	23.54	1.9 x 10^{29}

E_a increases with coated C.S. by Al$_2$O$_3$ in absence and presence PAA, it is obvious that thin layer of coat is playing a role in increasing the activation energy value, thereby indicating a more efficient inhibiting effect. According to eqn. (5) low values of A and high values E_a lead to lower corrosion rates. For the present study, there is some lower in the E_a values in presence of (0.1-0.5 %) PAA. Therefore, the decrease in the carbon steel corrosion rate is controlled by the pre-exponential factor A.

Thermodynamic studies

The values of thermodynamic parameters are presented in table 3 where the value of ΔG calculated from its dependence on corrosion potential (Eqn. 6).

$$\Delta G = -nFE_{corr}$$

$$(6)$$

The entropy (ΔS) and enthalpy (ΔH) are obtained from the slope and intercept respectively, of the plot of ΔG vs TΔS (Figure 10). The value of ΔG indicates that the coated C.S. functions by a chemical process on the surface of the metal. Generally, the values of ΔG up to -20 kJ mol^{-1} are consistent

with electrostatic interaction between charged molecules and a charged metal (physical process), while those more negative than -40 kJ mol^{-1} involve charge sharing or transfer from the inhibitor molecules to the metal surface, to from a co-ordinate type of bond (chemical process).[14]

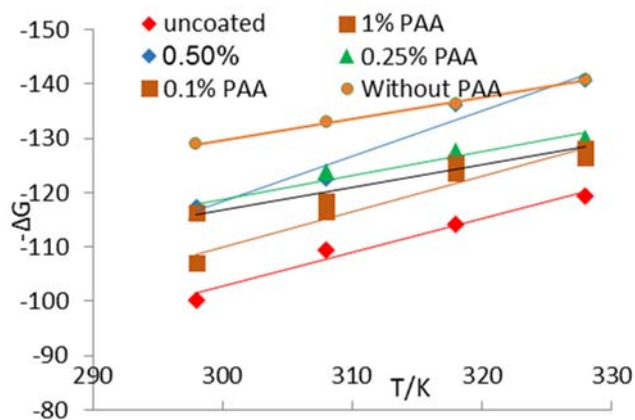**Figure 10.** Plot of -ΔG vs T for coated C.S. with Al$_2$O$_3$ NPs in absence and presence of different PAA % in 3.5 % NaCl.

Table 3. Thermodynamic parameter for the coated C.S..

	Conc.	-ΔG_{avg} kJ mol^{-1}	-ΔH_{avg} kJ mol^{-1}	-ΔS J K^{-1} mol^{-1}
Coated by Al$_2$O$_3$	Uncoated	110.86	304.55	618.6
	Without PAA	136.66	257.06	390.8
	(0.1%) PAA	122.17	254.22	421.9
	(0.25%) PAA	124.52	262.61	441.2
	(0.5%) PAA	129.24	389.53	831.6
	(1%) PAA	118.40	323.26	654.5

The negative sign of the ΔG obtained indicates that the process is spontaneous, while the negative sign of ΔS indicates that a process is accompanied by a decrease in entropy.[15]

Conclusion

Coating C.S. with alumina nanoparticles act as a good protecting thin layer to save it from corrosion, which give PE% reach to 82 %. The rate of corrosion increased with increasing temperatures ranged from 298 to 328 K. Adding PAA in suspension solution of coating act as stabilizer agent, which were adsorbed onto the surfaces of ceramic particles which, could generate steric and electrostatic stabilization and prevent particles agglomeration. PAA additives increase the PE % which reaches up to 87 % with 0.5 % of PAA. The surface porosity percentage, P %, generally increase with increasing temperature, and adding increasing amounts PAA increase the P % as P % depended on R_P and E_{corr}. The activation energy for the corrosion of coated C.S. is increased. The corrosion is a spontaneous and exothermic reaction (values of both ΔG and ΔH are negative). The AFM images of layer particles detection that Particles size increase after coated by different NPs in all cases.

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