

THE EFFECT OF SOME ORGANIC SURFACTANTS ON THE CORROSION OF ZINC IN NEUTRAL AND ALKALINE AQUEOUS SOLUTIONS

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Polarization and impedance measurements were carried out on a zinc electrode in neutral aqueous NaCl solutions and in alkaline aqueous KOH solutions containing organic corrosion inhibitors. The investigated inhibitors were sodium dodecylsulphate (SDS), sodium dodecylbenzenesulphonate (SDBS) and sodium 1,4-bis(2-ethylhexyl) sulposuccinate (AOT). The influence of these surfactants on the corrosion of zinc electrode in neutral solutions of NaCl was studied by measuring the current during hydrogen evolution.

The obtained results show that these surfactants inhibit the hydrogen evolution in neutral aqueous NaCl solutions and thus inhibit the corrosion process of zinc electrode. We presume that the surfactants are adsorbed on the zinc electrode surface and this adsorption process leads to a decrease in the rate of hydrogen evolution, thus allowing these compounds to be good substitutes for mercury and to be used for decreasing the electrode corrosion in batteries. In alkaline KOH solutions the adsorption of these surfactants can effectively depress the passivation of zinc surface during the electrochemical dissolution of zinc and therefore improve the discharge capacity of zinc anode in alkaline batteries.

INTRODUCTION

For long time zinc coatings have been used to protect iron against corrosion. These coatings act as a barrier and as galvanic protection. For these reasons the automobile industry has been using zinc coatings (on a large scale) to increase the duration of its ferrous metal structure. Galvanised steel is extensively used as material for roofs and facades and other equipments. Therefore, zinc metal is of great importance in various practical applications in different industrial fields.

Nowadays, zinc is widely used as high capacity anodic material for primary and secondary alkaline batteries because of its high specific energy, low cost and non-toxicity. However the high capacity of zinc anode can only be obtained in very concentrated alkaline solution. In dilute alkaline solutions the discharge capacity and power capability of zinc anode decrease dramatically with decreasing OH⁻ concentrations due to the passivation of zinc surface.

The passivation of zinc anode in dilute alkaline solution is known to result from the formation of passive film on zinc surface. It was shown by

Cabot and co-workers that the passivation of zinc takes place by a dissolution-precipitation mechanism and the dissolution of zinc is the rate-determining step.¹⁻² The passive film formed at the surface of zinc anode was postulated to consist of two layers: the outer layer is white and flocculent, formed by precipitation of the supersaturated zincate in the vicinity of the electrode surface. The inner layer is a dense ZnO film adhered on zinc surface and formed from the dehydration of the discharge product Zn(OH)₂, behaving as a barrier for further dissolution of zinc when it is formed.³ To suppress the anodic passivation and improve the usage of zinc, one usually use very concentrated alkaline solution to increase the solubility of ZnO or use electrolyte additives to modify the electrode surface to depress the blocking effects of the passive film on the diffusion of discharged zinc ions into bulk solution.⁴⁻⁷

However, most research works on the electrolyte additives were focused on the inhibition of zinc corrosion and dendritic formation in secondary zinc batteries.⁸⁻¹⁰ The effects of surfactant additives on the usage and discharge

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performances of zinc in dilute alkaline solution are rarely reported. This determined us to study the polarization of zinc in different media in the presence and absence of some organic corrosion inhibitors.

In this paper we studied the influence of some surfactants on the polarization behaviour of pure zinc in neutral and alkaline solutions.

EXPERIMENTAL

Polarization behaviour of pure zinc in aqueous solutions of NaCl and KOH was studied by potentiostatic and potentiodynamic methods and electrochemical impedance spectroscopy. The electrolytes used were 0.6M NaCl and 0.1M KOH. The following surfactants were used as organic inhibitors: sodium dodecyl sulfate (SDS), sodium dodecyl benzene sulfonate (SDBS), and sodium sulfosuccinate 1,4 bis [2-ethyl – hexyl] (AOT).

In all experiments the electrochemical polarization was started about 30 minutes after the working electrode was immersed in solution, to allow the stabilization of the stationary potential. Before each measurement, the potential of the working electrode was maintained at -1200 mV for 20 minutes, in order to remove the ZnO layer from the electrode surface. The working electrode potential was always measured with the reference to the saturated calomel electrode and was plotted against the current in external circuit obtaining the anodic or cathodic curves according to the variation of the working electrode potential. In order to reduce the ohmic resistance, we used a single compartment cell in which the working electrode was situated in the cell centre and surrounded by the auxiliary electrode, made of bright platinum gauze. This position allows the formation of a uniform and high electric field during the anodic or cathodic polarization. The determinations were repeated for each solution until a good reproducibility of the results was obtained. When plotting the polarization curves we deferred to the fact that prolonged anodic polarization might give rise to changes at the surface asperities level which would imply parallel translation of the Tafel slopes. This effect can be eliminated by first plotting the cathodic polarization curves and then the anodic ones - method used in the present paper.

RESULTS AND DISCUSSION

As it is well known, less active metals are less accessible and more expensive in comparison with ordinary metals which are too much exposed to corrosion process to be used. Protection of these metals can be achieved by multiple ways from which the treatment of the corrosive media is one of the most important. The treatment of the corrosive media can be achieved by removing the aggressive chemical agent or by using inhibitors that control the corrosion acting over the anodic or cathodic reaction or both. Here, the inhibition of corrosion is the result of the adsorption of the

organic compound on the metal surface forming an invisible film a few molecular diameters thickness.

The used inhibitors were sodium dodecyl sulfate (SDS), sodium dodecyl benzene sulfonate (SDBS), and sodium sulfosuccinate bis [2-ethyl – hexyl] (AOT), for which it was determined the CMC (critical micelle concentration) by the surface tension and the equivalent electric conductivity methods. The tensioactive properties of these three organic substances were pointed out by the study of their behaviour in aqueous solutions at different concentrations of the organic substances. The solutions were prepared with double-distilled water and were kept in dark bottles for eight or ten hours in order to reach the surface equilibrium. The variation of specific conductivity with the concentration of the tensioactive substance was determined at constant temperature of 25 °C by the conductometric method. The determination of the surface tension was made by the method of taking out the ring off the surface of the solution, using a torsion balance which had the ring attached to its arm. All of these determinations were made with the purpose of characterizing the physico-chemical properties of the previous surfactants in aqueous environments.

The tensioactive and colloidal properties of the surfactants are given by the amfifilic nature of the studied surfactants came out due to the presence in their molecule of groups with different affinities to the solvent (hydrocarbonate group is hydrophobic and ionic and non-ionic groups are hydrophilic).¹¹⁻¹³ It is well known that the CMC represents the range of the concentration in which the surfactants, in solution, change their initial molecular solvated state (nonaggregate) in the aggregate dispersive state. The aggregates or colloidal micelles are formed from a variable number of molecules, ranging from tens to hundreds molecules. The CMC is influenced by a series of factors dependent of the surfactant nature, the nature of the aqueous dispersion environment and of the method used for determination. The main importance of the determination of the CMC consists in the fact that at this concentration, most of the physico-chemical properties of the surfactant solution present an instant variation.

The determined CMC values were: $7.8 \cdot 10^{-3}$ M for SDS, $1.4 \cdot 10^{-3}$ M for SDBS and for AOT $2.2 \cdot 10^{-3}$ M.

From the variations of the surface tension and equivalent conductivity with concentration for the three tensioactive substances we concluded that, under CMC value, all three substances behave as mono-monovalent electrolytes strongly dissociated,

while at concentrations greater than CMC, they form colloidal micelles which turn into micellar aggregates with the increasing of the concentration.

Further, it has been studied the influence of these surfactants on the polarization of zinc in aqueous solution of 3.5% NaCl.

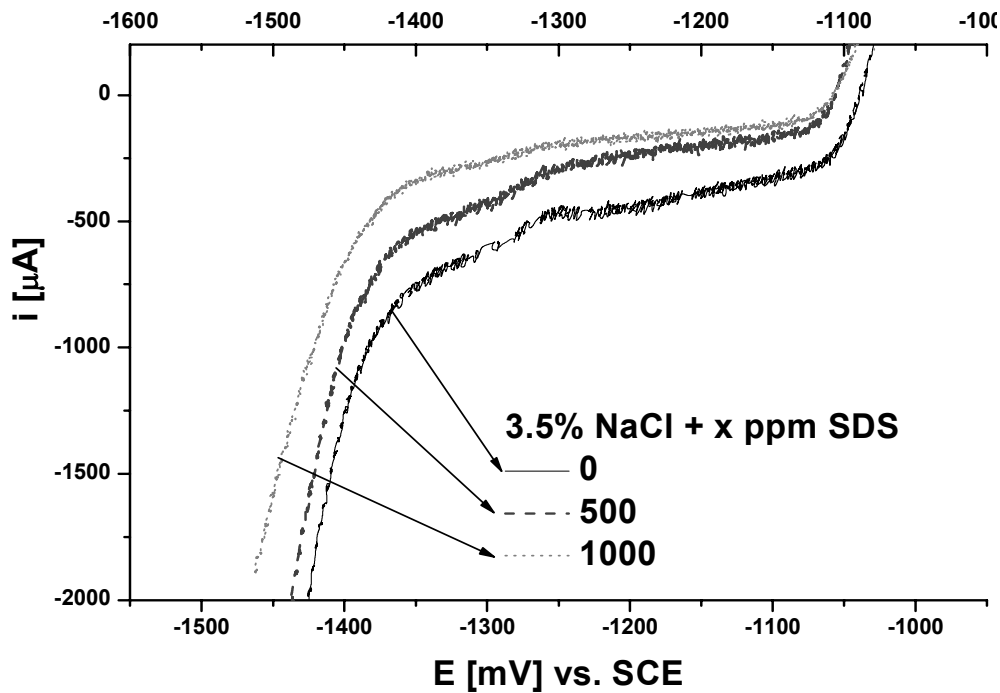


Fig. 1 – Cathodic polarization curves of zinc in aqueous solutions of 3.5% NaCl + x ppm SDS, at 25°C.

Because in the tables 1, 2 and 3 are given all the kinetic parameters of corrosion obtained from the polarization curves, in figure 1 will be given only a few characteristic cathodic polarization curves. We

recorded only the cathodic curves because the surfactants act as cathodic inhibitors especially in case of zinc in according to the data from literature.^{4, 14-15}

Table 1

Kinetic parameters of corrosion for pure zinc in aqueous solutions of 3.5% NaCl + x ppm SDS, at 25°C

C_{SDS} [ppm]	I_{H_2} at -1385 mV [μA]	θ	E [%]
0	-1033	-	-
20	-892	0.136	13.6
50	-886	0.1423	14.23
75	-878	0.150	15.00
100	-820	0.2062	20.62
150	-781	0.2439	24.39
200	-759	0.2652	26.52
300	-700	0.3223	32.23
400	-695	0.3272	32.72
500	-663	0.3581	35.81
1000	-520	0.4966	49.66
1500	-504	0.512	51.20
2000	-487	0.528	52.8
2500	-482	0.5334	53.34

Analyzing the data from figure 1 and table 1 it can be observed that an inhibition of the hydrogen evolution takes place in all cases of SDS surfactant addition. This is observed by the decreasing of hydrogen evolution current and increasing of the hydrogen evolution overvoltage. The maximum efficiency of the inhibition action of the SDS surfactant is observed at concentrations equal or close to CMC value.

Further, we studied the inhibition action of the second surfactant on the corrosion of pure zinc in 3.5% NaCl solution. Cathodic polarization curves were plotted from which kinetic parameters of corrosion were determined e.g. hydrogen evolution current at a given potential and the efficiency of cathodic process inhibition.

Analyzing the data presented in table 2, one can see that the SDBS addition at given concentrations

lead in all cases to the inhibition of cathodic hydrogen evolution and therefore at the inhibition of overall corrosion, meaning a decreasing of the corrosion rate. It is also observed that the maximum efficiency of cathodic hydrogen evolution corresponds to concentrations equal or close to CMC value for SDBS.

Finally, we studied the influence of the AOT surfactant and the experimental results are presented in table 3. Similarly to the previous cases, the AOT addition leads to the inhibition of corrosion and increasing of hydrogen evolution overvoltage and decreasing of corresponding current, respectively. The maximum inhibition efficiency was observed at surfactant concentrations equal or close to its CMC value.

Table 2

Kinetic parameters of corrosion for pure zinc in aqueous solutions of 3.5% NaCl + x ppm SDBS, at 25°C

C_{SDBS} [ppm]	I_{H_2} at -1385 mV [μA]	θ	E [%]
0	-1033	-	-
20	-1011	0.021	2.12
50	-944	0.086	8.61
100	-866	0.162	16.16
150	-800	0.226	22.55
200	-789	0.236	23.62
300	-620	0.399	39.98
400	-472	0.543	54.30
500	-418	0.595	59.53
1000	-420	0.5934	59.34
1500	-434	0.5798	58.00
2000	-437	0.576	57.60

Table 3

Kinetic parameters of corrosion for pure zinc in aqueous solutions of 3.5% NaCl + x ppm AOT at 25°C

C_{AOT} [ppm]	I_{H_2} at -1385 mV [μA]	θ	E [%]
0	-1033	-	-
75	-931	0.098	9.87
100	-610	0.409	41
150	-594	0.424	42.4
200	-585	0.433	43.30
300	-583	0.435	43.50
500	-55	0.467	46.70
1000	-528	0.488	48.80
1500	-500	0.516	51.60
2000	-514	0.502	50.2
2500	-517	0.4995	49.95

The inhibition action can be explained by the surfactant adsorption at the solid / liquid interface. This process depends not only on the surfactant solution properties but also on the solid / liquid interface properties and the interactions between the various dissolved species. The orientation of the surfactant at the solid-liquid interface is determined by the hydrophobic/hydrophilic character of the solid. On hydrophobic surfaces, surfactants adsorb with their hydrophobic tails towards the surface, making the surface hydrophilic nature. On hydrophilic surface surfactants will usually adsorb with their hydrophilic groups towards the surface depending on the surface chemical and electrochemical properties of the solid (i.e. charge characteristics). In some cases (high values of surfactant concentrations) a double layer of adsorbed surfactant may form.

In this case, inhibition efficiency is the highest. This can be explained on the basis that a bimolecular layer forms at the electrode / solution interface. The free energy of the adsorption of surfactants at the solid-liquid interface can be considered to be the sum of a number of contributing factors such as hydrogen bonding, electrostatic and hydrophobic interactions and specific interactions such as covalent bonding:

$$\Delta G_{\text{ads}} = \Delta G_{\text{elect}} + \Delta G_{\text{H}} + \Delta G_{\text{hydrofobic}} + \Delta G_{\text{specific}} + \dots$$

Note that adsorption can occur as long as the net free energy changed involved in the adsorption is negative even if some of the factors oppose the adsorption. In this case, we presume that the inhibitors of this type are strongly adsorbed on the metal surface resulting in a protector film on the metal surface and therefore the reaction between the metal and the corrosion solution would take place only through the diffusion of the ions of the aggressive medium through the fines pores of the protector film which has been formed. The adsorption is stronger after the CMC is reached. This fact explains the highest inhibitor efficiency at concentrations equal or close to its CMC value. In this way we can explain the strong decreasing of the corrosion rate after reaching of the CMC and thus the high efficiency of these three inhibitors.

Further, the influence of the three anionic surfactants on the polarization behaviour of pure zinc was studied in diluted KOH solutions. It is well known that zinc is widely used as a high capacity anodic material for primary and secondary alkaline batteries. The high capacity of zinc anode can only be obtained in very concentrated alkaline solution. In dilute alkaline solutions, the discharge

capacity and power capability of zinc anode decrease dramatically with decreasing OH^- concentrations due to the passivation of zinc surface.

The passivation of zinc anode in dilute alkaline solution is known to result from the formation of passive film on zinc surface. In past decades, numerous works have been undertaken to evaluate the anodic passivation mechanism and the properties of the passive film of zinc electrode in alkaline solution.^{1-4,8,16} It is now well agreed that the passivation of zinc takes place by a dissolution-precipitation mechanism and the dissolution of zinc is the rate-determining step.¹⁻² The passive film formed at the surface of zinc anode was postulated to consist of two layers: the outer layer is white and flocculent, formed by precipitation of the supersaturated zincate in the vicinity of the electrode surface. The inner layer is a dense ZnO film adhered on zinc surface and formed from the dehydration of the discharge product $\text{Zn}(\text{OH})_2$, behaving as a barrier for further dissolution of zinc when it is formed.³ To suppress the anodic passivation and improve the utilization of zinc, one usually use very concentrated alkaline solution to increase the solubility of ZnO or use electrolyte additives to modify the electrode surface to depress the blocking effects of the passive film on the diffusion of discharged zinc ions into bulk solution.⁴⁻⁷ Most research works on the electrolyte additives were focused on the inhibition of zinc corrosion and dendritic formation in secondary zinc batteries.^{8-10,17-18} The effects of surfactant additives on the utilization and discharge performances of zinc in dilute alkaline solution are rarely reported. This is the reason for which we studied the addition effects of the three anionic surfactants on the polarization behaviour of pure zinc in aqueous solutions of 0.1 M KOH.

In figure 2 are given for exemplification a few characteristic cathodic polarization curves in aqueous solution of 0.1M KOH with and without SDS additions. The kinetic parameters corresponding to this system are given in table 4.

Analyzing the data from table 4, we can see that, in this case the surfactant action is reversed to the one in the system $\text{Zn} + 3.5\% \text{NaCl}$. The SDS addition lead to increasing of hydrogen evolution current and therefore to decreasing of hydrogen evolution overvoltage. It can be also seen that hydrogen evolution overvoltage decrease with increasing surfactant concentration, the lowest values corresponding to concentrations equal or close to CMC.

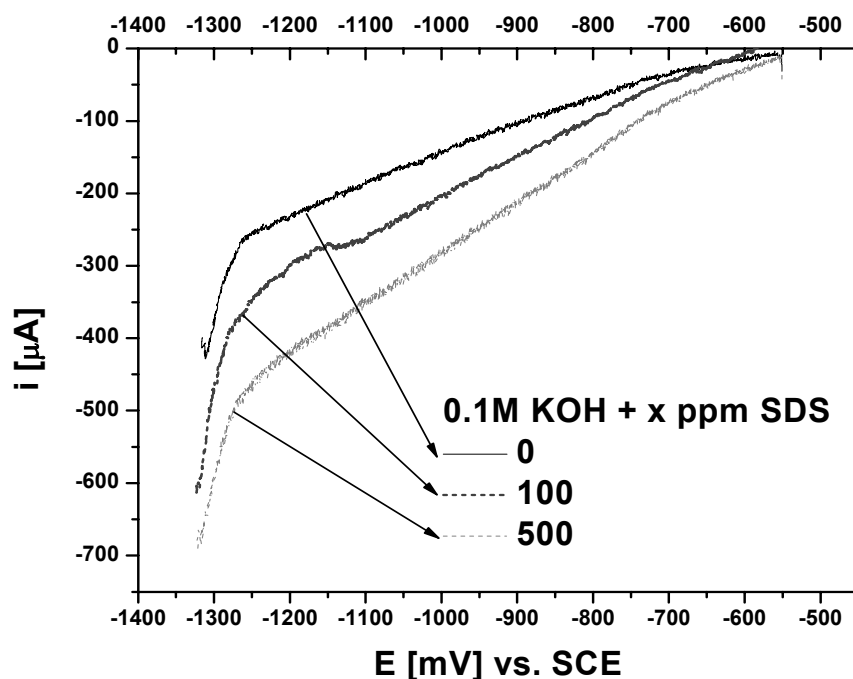


Fig. 2 – Cathodic polarization curves of zinc in aqueous solutions of 0.1 M KOH + x ppm SDS at 25°C and 1 mV s⁻¹ sweep rate.

Table 4

Kinetic parameters of corrosion for pure zinc in aqueous solutions of 0.1M KOH + x ppm SDS at 25°C and 1 mV s⁻¹ sweep rate

c_{SDS} [ppm]	I_{H_2} , at -1250 mV [μA]	$I_{\text{H}_2} / I_{\text{H}_2}^0$
0	-253	-
50	-256	1.01
75	-279	1.102
100	-345	1.36
200	-355	1.403
500	-459	1.814
1000	-568	2.245
1500	-573	2.265
2000	-580	2.29
2500	-594	2.347

Similar behaviour is observed for the other two anionic surfactants. Experimental data are presented in tables 5 and 6. Again, it can be observed the increasing of hydrogen evolution current and decreasing of hydrogen evolution overvoltage with increasing of surfactant concentration. The maximum is observed at surfactant concentration values close to CMC.

We can say that decreasing of hydrogen evolution overvoltage and increasing of hydrogen evolution current are maximum at concentrations equal or a little higher than CMC. This behaviour can be explained by the less adherent and porous passive film formed at zinc surface in the presence of the three surfactants. Although these surfactants adsorption at zinc surface takes place in almost all

active sites and impedes the charge transfer thus increasing the polarization resistance that leads to a sluggish kinetics of interfacial reaction, sweeping the electrode potential in anodic direction leads to increasing anodic diffusion current or increasing hydrogen evolution current with reference to free surfactant electrolyte in the case of cathodic sweeping of the potential.

The sluggish kinetics of interfacial reaction and increased diffusion (or hydrogen evolution) current for zinc in the surfactant containing electrolyte seem to be conflict, but this could be explained by the formation of a loose and porous passive film on the zinc surface in the presence of surfactants in the electrolyte.

Table 5

Kinetic parameters of corrosion for pure zinc in aqueous solutions of 0.1M KOH + x ppm SDBS at 25°C and 1 mV s⁻¹ sweep rate

C _{SDBS} [ppm]	I _{H₂} , at -1250 mV [μA]	I _{H₂} ¹ / I _{H₂} ⁰
0	-253	-
20	-256	1.01
50	-261	1.03
75	-314	1.24
100	-386	1.52
200	-400	1.58
400	-427	1.68
500	-444	1.75
750	-498	1.97
1000	-517	2.04
1500	-520	2.055
2000	-539	2.13
2500	-570	2.25

Table 6

Kinetic parameters of corrosion for pure zinc in aqueous solutions of 0.1M KOH + x ppm AOT at 25°C and 1 mV s⁻¹ sweep rate

C _{AOT} [ppm]	I _{H₂} , at -1250 mV [μA]	I _{H₂} ¹ / I _{H₂} ⁰
0	-253	-
50	-381	1.5
75	-391	1.545
100	-494	1.95
200	-500	1.976
400	-512	2.02
500	-564	2.23
750	-574	2.26
1000	-592	2.34
1500	-598	2.36
2000	-604	2.39
2500	-619	2.45

Although the mentioned surfactants adsorption can reduce the active surface area and the anodic dissolution rate of zinc, this could be compensated by the enhanced diffusion rate for the reactant and discharged product through the less compact passive film brought about by the adsorption of surfactants. It can be said that SDS, SDBS and AOT additions in dilute alkaline solutions can effectively depress the passivation of zinc surface during the electrochemical dissolution of zinc and therefore improve the discharge capacity of zinc anodes in alkaline batteries. The suppression effect is suggested to result from the adsorption of the electrolyte additive, which produces a loose and porous passive film at the zinc surface, fact also put in evidence by our results.

In order to further investigate the polarization behaviour of pure zinc in 0.1M KOH with and without inhibitors, impedance spectroscopy was used to follow the interfacial properties of the electrode. The formation of the oxide barrier film

which impedes the charge transfer reaction and the action of the adsorbed inhibitor on the corrosion rate were the main processes observed by Faradaic impedance spectroscopy.

Figure 3 shows the Nyquist plots for the zinc electrode in 0.1M KOH with and without inhibitor. To give more detailed information about the electrical properties of the above system, the Randles circuit (inset of the fig. 3) was chosen to fit the obtained impedance data. In the Randles circuit, the resistance to electron transfer (R_p) and the diffusion impedance (Z_w) were assumed to be parallel to the interfacial double layer capacity (C_{dl}). The parallel combination of R_p and C_{dl} give rise to a semicircle in the Nyquist plot of Z_i versus Z_r . In the Nyquist plot, the semicircular part observed at higher frequencies corresponds to the electron transfer limited process, whereas the linear part is characteristic of the lower frequencies range and represents the diffusion-limited electron transfer process.

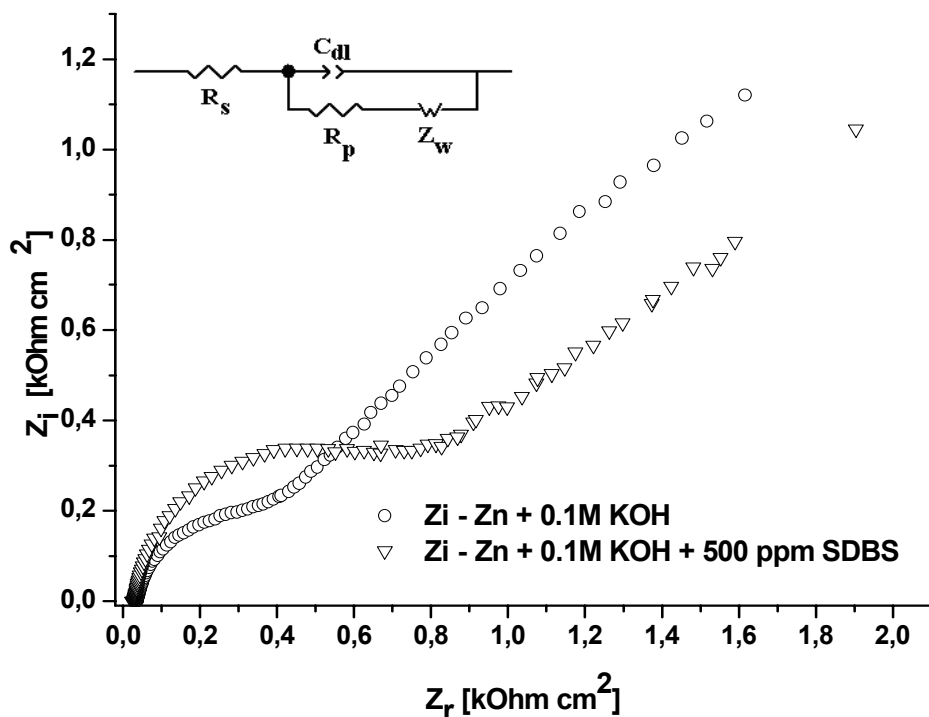


Fig. 3 – The Nyquist plot for the zinc electrode in 0.1M KOH electrolyte with and without inhibitor at open circuit potential.

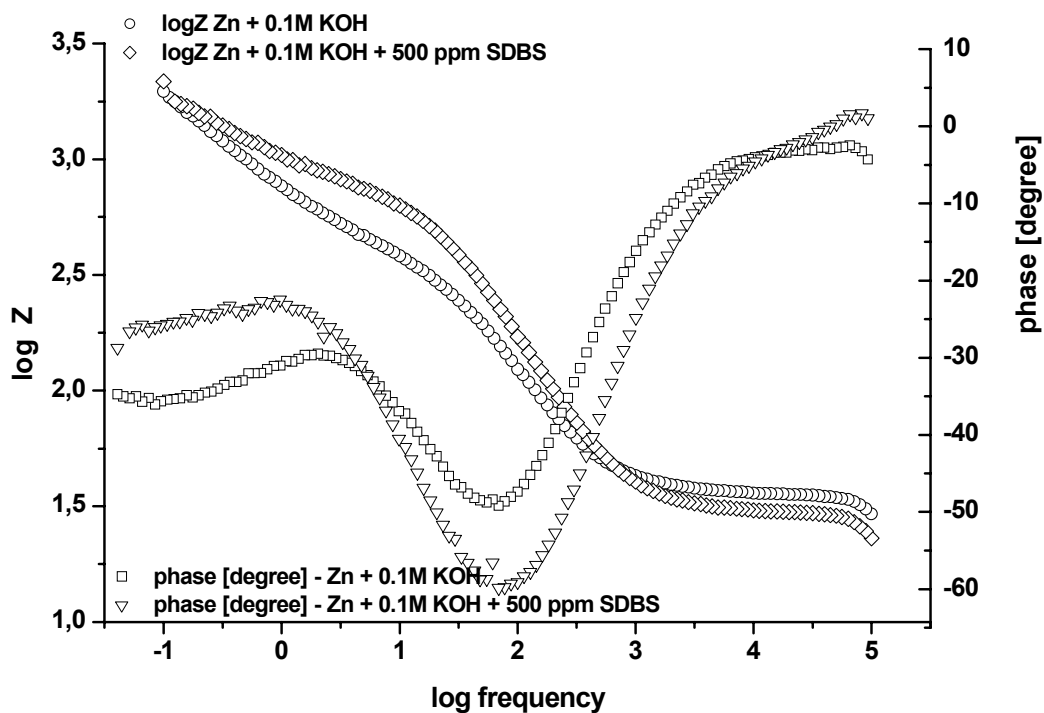


Fig. 4 – The Bode plot for zinc electrode in 0.1M KOH electrolyte with and without inhibitor at open circuit potential.

It can be seen from figure 3 that, after the addition of the organic surfactant, the semicircle diameter is much larger than in the case of free surfactant electrolyte. This fact suggests that the

organic inhibitor was adsorbed on the surface electrode and impedes the charge transfer reaction. From Bode diagram (see fig. 4) we can conclude that our system presents the same behaviour.

CONCLUSIONS

In the aqueous solutions of 3.5% NaCl all three anionic surfactants (SDS, SDBS and AOT) lead to inhibition of cathodic process by decreasing the hydrogen evolution current and therefore increasing the hydrogen evolution overvoltage.

The inhibition effect of the given organic compounds can be attributed to the fact that they are strongly adsorbed at the metal surface by various interactions resulting in a protective film at the metal surface that hinders the corrosion. The inhibition action of each surfactant reaches a maximum at concentrations equal or close to critical micelle concentration.

In dilute KOH solutions, the surfactants addition lead to decreasing hydrogen evolution overvoltage and increasing corresponding current, respectively. The activation of cathodic hydrogen evolution can result from the less adherent and porous passive film formed at zinc surface in the presence of the three surfactants.

The hydrogen evolution overvoltage decreased with increasing surfactant concentration. The lowest values corresponded to concentrations equal to or slightly higher than critical micelle concentration.

SDS, SDBS and AOT additions in dilute alkaline solutions can effectively depress the passivation of zinc surface during the electrochemical dissolution of zinc and therefore improve the discharge capacity of zinc anodes in alkaline batteries.

The impedance spectroscopy data revealed a semicircular part at higher frequencies corresponding to the electron transfer limited process and a linear

part characteristic of the lower frequencies range representing the diffusion-limited electron transfer process.

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