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Corrosion study of cola soft drink cans

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Abstract. The study of corrosion in aluminum packaging is fundamental to ensure the quality and safety of the product. The varnish layer existing on metal packaging aims to minimize any interaction between the food or drink and the metal, as well as minimizing the corrosion process. The acidic nature of soft drinks, as well as the ions existing in solution, such as phosphates, benzoates or chlorides, play an important role in the oxidative process of aluminum. This study evaluated the corrosion of the body of aluminum cola cans. The beverage was first characterized and the results obtained were: pH =2.5; 7.5 ºBrix; chloride concentration of 0.17g/L, acidity 0.17 %m/m; density 1.04 g/mL and concentration of reducing sugars was 11.3 %m/m. The corrosion of aluminum in model solutions with different concentrations of citric acid and NaCl was studied via linear polarization for samples with and without varnish. The statistical analysis carried out, via factorial design 2^3 with a triplicate at the center point, showed that the corrosion rate (CR) of the sample with varnish was significantly influenced by temperatures above 45ºC in the range of chlorides studied. On the other hand, the CR of the sample without varnish was strongly influenced by the combination of high temperatures and high chloride concentrations. When the varnish was removed with acetone and then polished with sandpaper it resulted in a higher activation energy (AE=67.48kJ/mol) when compared to the sample with varnish (AE=88.92kJ/mol). From a kinetic point of view, this showed the protective effect of this layer and its effectiveness against corrosion. The ΔH^{o} and ΔG^{o} activation parameters of the process were positive, showing that corrosion is an endothermic process with increased disorder when the varnish is removed. It is therefore important to buy the product with the packaging in good condition to guarantee the integrity of the protective layer and its quality, since oxidation of the aluminum can lead to products that compromise the quality of the food or drink.

Keywords: Electrochemical corrosion, aluminum, cola soft drinks, linear polarization

Introduction

Packaging has the function of protecting the product from external actions such as contamination, thus preventing deterioration and facilitating its transport and storage (Robertson, 2009; Jorge, 2013).

Among the various types of packaging, aluminum is the most commonly used for packaging beverages. According to data estimated by Grand View Research (2020), in 2023, the global market for cans was USD 41.14 billion, with indications of an increase in the following years.

Advantages such as lighter weight, impermeability, high mechanical resistance and recyclability are some of the factors that contribute to the application of aluminum in the food industry. However, although the surface layer of aluminum oxide (Al_2O_3) protects the metal, in acidic environments (pH <4.5) such as that of cola drinks this material is unstable, leading to corrosion. This process leads to the dissolution of the metal and the formation of Al^{3+} ions.

Furthermore, in the presence of chloride (Cl^-), corrosion (pitting) can be even more severe, leading to deterioration of the oxide layer, even in a neutral environment where the protective layer is stable (Taroco et al, 2020; Reis et al, 2018; Soares et al, 2016; Bakos and Szabó, 2008). The dissolution of aluminum in these packages is not a simple process and involves the formation of soluble complexes between Al^{3+} and citrate or phosphate ions present in soft drinks, or even insoluble salts such as aluminum phosphate ($AlPO_4$). The formation of these complexes has a strong influence on corrosion[8,9].

To avoid or minimize this process as much as possible, aluminum cans are coated with a layer of varnish that protects the packaging from the interaction of the beverage with the metal. In this sense, it is important that this layer is intact so that its efficacy is secured.

In addition to the varnish and the formation of possible salts and complexes, other factors are important and should be studied, as they can influence the corrosion of the packaging, such as: the pH of the medium, chloride concentration, storage temperature or transport. These parameters, as well as the influence of each and their interactions on the corrosion of aluminum cola cans, will be addressed in this work via electrochemical measurements.

Material and Methods

Physical and chemical characterization of cola soft drinks

Samples of cola soft drinks from pet bottles of the same batch and from the same manufacturer were analyzed. The pH was determined using a Hanna pH meter (model HI 5222) and the °Brix using an Abee refractometer. Density was determined using a pycnometer. The acidity of the soft drink was obtained using potentiometric titration, while the concentration of chloride (Cl^-) was obtained using argentometric titration. The concentration of reducing sugars present was also calculated using the Lane Eynon determination (Lane and Eynon, 1923). All determinations were carried out in triplicate.

Electrochemical measurements

Working electrodes were made from cola cans, with an active area of $1cm^2$. Electrodes with and without varnish were used. Acetone and absorbent cotton were used to remove the protective layer and to determine the activation energy, the varnish was also removed with acetone and then the electrode was sanded using 180 grit sandpaper and then washed with distilled water.

The electrochemical measurements, via linear polarization, were carried out in an AutoLab potentiostat (PGSTAT 200). A scan rate of 0.5 mVs^{-1} was used in the potential range from -0.05 V to 0.15 V. The current (i_c) and corrosion potential (E_c) were determined from the intersection of the anodic and cathodic curves using the NOVA software, as shown in figure 01. The corrosion rate (CR) is obtained using equation 1.

$$CR = \frac{ic\,MM}{Z\,F\,d}$$

(equation 1)

Where:
ic: corrosion current density (A/cm^2);
MM: molar mass (g/mol);
Z: electrical charge of the dissolved metal (for the case under study: 3^+);
F: Faraday constant (96.500 C/mol)
d: density of the material (Fe = 2.699 g/cm^3)

A three-electrode electrochemical cell was used for the electrochemical measurements: Ag/AgCl as the reference electrode, platinum as the auxiliary electrode and the body of the can as the working electrode.

The model solutions were used as electrolytes in conditions close to cola soft drink. The model solutions with different conditions were used in the 11 factorial design experiments for the statistical study and verification of the influence of temperature, citric acid and chloride concentration on the response variable, which was the corrosion rate.

To evaluate chloride concentrations, model solutions were also used at concentrations of 0.5, 1.0, 3.0 and 5.0 g/L, at 25 °C, for 0.17% m/m citric acid (citric acid concentration of the soft drink under study).

For the temperature variation, a water bath and an ice bath were used for the solutions with 0.17% m/m and 0.05 g/L. These analyses were carried out on the soft drink can samples with and without varnish.

Statistical analysis

A central composite design (CCP), together with the response surface methodology, was used to evaluate the influence of the independent variables, Cl^- concentration, temperature and citric acid concentration, on the corrosion rate (CR). The 2^3 factorial with 3 central points and its axial extension were used, whose factor levels and their coded values are shown in Table 1.

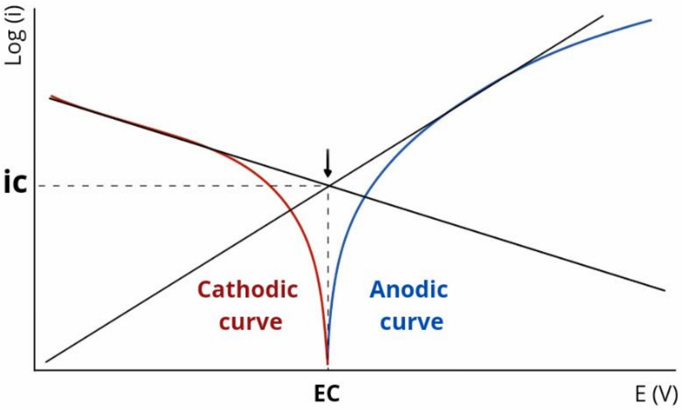


Figure 1. Intersection of anodic and cathodic Tafel curves for determining corrosion current and potential.

Table 1. Levels for the factors and their coded values

Variables	Low level (-)	Central Point	High level (+)
Citric acid (%m/m)	0.17	0.35	0.5
Cl^- (g/L)	0.05	0.2	0.35
Temperature (°C)	25	35	45

The effect of the main, linear and/or quadratic factors and their interactions were evaluated using analysis of variance (ANOVA) at a 5% significance level. The statistical analyses were carried out using Statistica software (JPZ804I6009FA-9), version 13.

Results and discussion

The soft drink's physical and chemical characteristics

The results obtained from the physicochemical characterizations of the cola soft drink are shown in Table 2.

Although it contains phosphoric acid, which is commonly used in cola drinks, the acidity was expressed as citric acid, as determined by law no. 544/1998 (Brasília, 1998).The presence of phosphoric acid has a major influence on pH, resulting in a more acidic pH when compared to other carbonated drinks. At a pH below 4.5 (like that of the beverage studied) the surface aluminum oxide layer such as Al_2O_3 or $Al_2O_3.H_2O$ is unstable, making the corrosion process more favorable (Soares et al, 2017; Mayouf et al, 2008).

Table 2. Physicochemical parameters of cola from pet bottles.

pH	°Brix (%)	Cl^- (g/L)	Acidity (% m/m)	Density (g/L)	Reducing sugars (% m/v)
2.40	7.5	0.17	0.17	1.04	11.2

Electrochemical measurements

Scanning rate study

Figure 2 shows the influence of corrosion on the scanning rate during electrochemical measurements. The current observed in the electrochemical system that produces the corrosion rate can be due to the capacitive current (i_{cap}) and the faradaic current (i_{Far}) (equation 2). Equation 3 shows that C corresponds to the capacitance of the electrode/solution interface and S represents the potential scanning rate. It can be seen that as the scanning rate (S) increases, the current increases linearly. However, for scanning rates below 1mV/s, the corrosion rate does not vary significantly. Therefore, a scanning rate of 0.5 mV/s was chosen for the linear polarization tests to determine the corrosion rate.

$$i = i_{cap} + i_{Far} \quad \text{(equation 2)}$$

$$i = CS + i_{Far} \quad \text{(equation 3)}$$

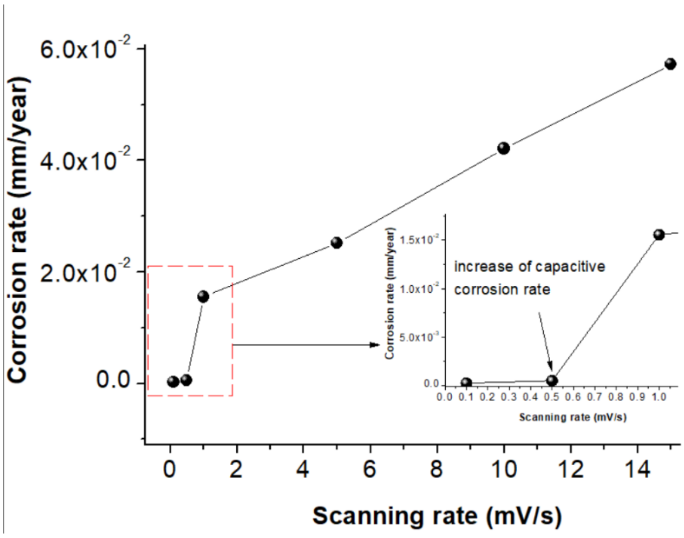


Figure 2. Corrosion rate as a function of scanning rate for the aluminum electrode in the medium of the soft drink.

Influence of chloride concentration

The chloride concentration influence in corrosion is shown in figure 03.

As the concentration of chloride (Cl-) increases, the corrosion rate increases. Cl-, an ion present in many drinks, is highlighted as one of the main compounds that contribute to the corrosion process, causing pitting corrosion (Bakos and Szabó, 2008; Solmaz et al, 2008).

Corrosion of aluminum through the presence of chloride ion can be represented by the following mechanism, as proposed by Soares and collaborators (Soares, 1994).

$Al \rightarrow Al^{3+} + 3e^-$ (equation 4)

$Al^{3+} + Cl^-_{(sol)} \rightarrow AlCl^{2+}_{(ads)}$ (equation 5)

$AlCl^{2+}_{(ads)} + 2Cl^-_{(sol)} \rightarrow AlCl_{3(ads)}$ (equation 6)

$AlCl_{3(ads)} + Cl^-_{(sol)} \rightarrow AlCl^-_{4\ (sol)}$ (equation 7)

The first stage of corrosion is the oxidation of Al (equation 4). After this, the Al^{3+} ions react with the interfacial Cl- ions to form complexes according to equations 5, 6 and 7. With the formation of the soluble AlCl-4 complex, present in the solution, the passivation layer breaks down, favoring corrosion (Solmaz et al, 2008; Ambat, 1994).

Considering the concentration of citric acid and its ka value, the pH of the solution is close to 2.8. Thus, the first ionization of citric acid is shown in equation 8. Equation 9 represents the adsorption of H^2Cit- ions at the electrode/solution interface. The presence of H_2Cit- ions in the solution studied can cause the oxide film (Al_2O_3) to dissolve. In addition, competition between the anions from equation 5 and the anions generated by the adsorption and desorption of citrate on the metal surface can generate a corrosion rate with mixed behavior (Solmaz at al, 2008).

$H_3Cit \rightarrow H_2Cit^-_{(sol)} + H^+$ (equation 8)

$H_2Cit^-_{(sol)} \rightarrow H_2Cit^-_{(ads)}$ (equation 9)

$Al_2O_3 + 2H_2Cit^-_{(ads)} + 2H^+ \rightarrow 2AlCit_{(sol)} + 3H_2O$ (equation 10)

According to Solmaz, the pH_{zch} value (zero charge point) for aluminum is 9.1. Thus, at acidic pHs, the surface charge of aluminum is positive, favoring the adsorption of Cl^- anions and Cit^{-1} anions on the metal's surface (Seruga and Hasenay, 2001). Although chloride ions promote corrosion, the H_2Cit^- anions adsorbed on the metal surface (equation 10) reduce the availability of Al^{3+} ions and consequently reduce the CR.

The b_a and b_c values obtained from the Taffel curve fitted for the minimum chloride concentration evaluated (0.5 g/L) were 112.97 mV/dec and 19.59 mV/dec, respectively. While for the highest concentration (5.0 g/L), the values obtained were 273.92 mV/dec and 44.403 mV/dec for b_a and b_c respectively. As observed by Seruga and Hasenay (1996), the ba values higher than expected (which would be 40mV/dec) correspond to the uniform anodic dissolution of Al, as well as the growth of the aluminum oxide film formed on the electrode surface during anodic polarization.

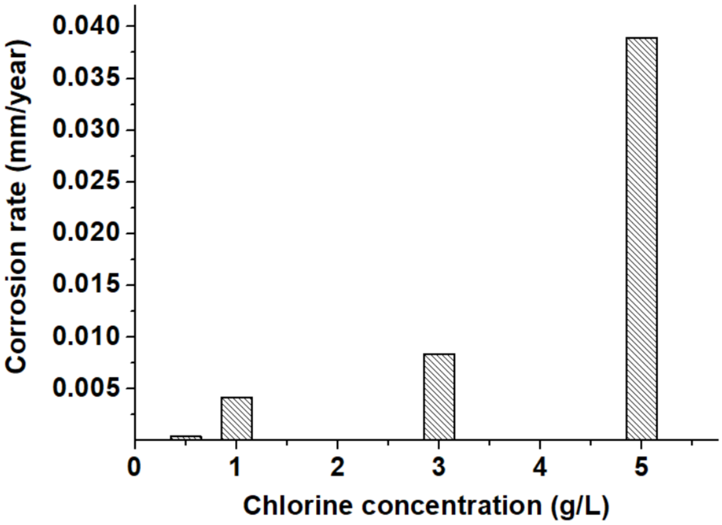


Figure 2. Corrosion rate as a function of chloride concentration in a 0.17% m/v citric acid solution.

Thermodynamics parameters

Figure 4 shows the variation in CR for the samples with and without varnish. Over the entire temperature range studied, it can be seen that the samples without varnish have higher corrosion rate values, as expected. This is due to the increased diffusion of molecules and ions in solution, which break the activation barrier, favoring corrosion[4,5,16,17]. (Taroco et al, 2020; Rahayu and Asmorowati, 2019; Reis et al, 2018; Addia et al, 2018).

With the corrosion rate (proportional to k) obtained with the temperature variation, it is possible to find the value of the Activation Energy of the reaction, based on the Arrhenius equation (Equation 11).

$$\ln k = \ln A - \frac{Ea}{RT} \qquad \text{(equation 11)}$$

Table 3 shows the activation energy values for the soft drink can samples with and without varnish, as well as the angular coefficient and R^2 value obtained from the linear regression (figure 5). Tests were carried out with different ways of removing the varnish: with acetone alone and with acetone and subsequent sanding using 180 grit sandpaper.

The activation energy increases when the varnish layer is removed, indicating that the corrosion process is favored by the removal of the protective layer. The electrochemical measurements carried out show that sanding the sample led to even more effective removal of the varnish layer.

Using the modified Arrhenius equation (equation 12) and the graph of ln(K/T) as a function of 1/T, the variation in activation enthalpy (ΔH°) and the variation in activation entropy (ΔS°) of the corrosion process were obtained, with the angular and linear coefficients, respectively (Akinbulumo et al, 2020). The data is shown in Table 4.

$$\ln \frac{K}{T} = -\frac{\Delta H}{RT} + \frac{\Delta S}{R} + \ln \frac{R}{Nh} \qquad \text{(equation 12)}$$

It can be seen that the variation in the enthalpy of activation of the corrosion process (ΔH°) is positive in all cases, showing that the metal dissolution process is endothermic. The positive values of the variations in the entropies of activation of the corrosion process (ΔS°) are positive and increase with the removal of the varnish, especially in the case where the protective layer was removed with acetone and sandpaper, which shows the increase in disorder at the electrode/solution interface due to the increase in the number of degrees of freedom (Akinbulumo et al, 2020; Rahiman and Sethumanickam, 2017).

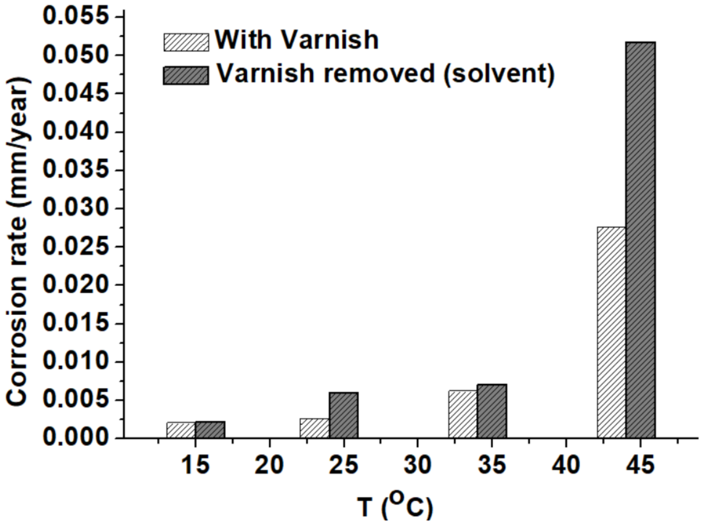


Figure 4. Corrosion rate at different temperatures for samples with and without varnish.

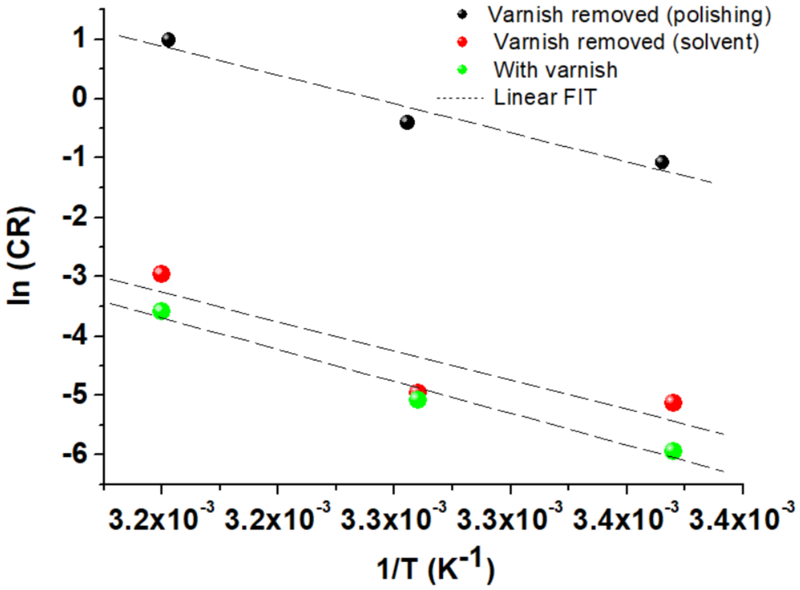


Figure 5. Ln CR as a function of the reciprocal of the absolute temperature for samples with and without varnish.

Table 3. Activation energy and linear fit parameters in the curves in Figure 5.

Sample	Angle coefficient	Activation energy (kJ/mol)	R^2
With varnish	-10695.7273	88.92	0.98863
Without varnish (acetone)	-9839.9091	81.81	0.89914
Without varnish (acetone + sanded)	-9700.8748	67.48	0.97657

Table 4. Thermodynamic parameters of the samples with and without varnish.

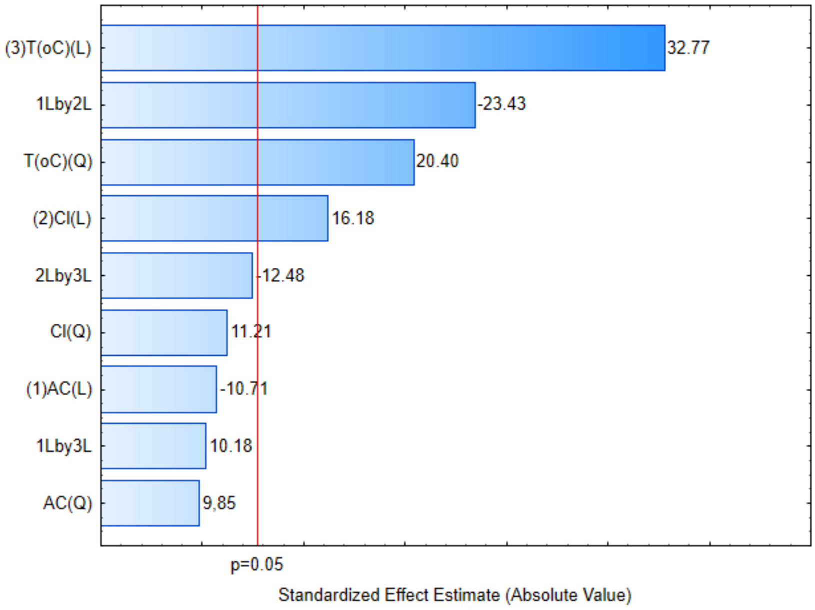
Sample	ΔH^o (kJ.mol^{-1})	ΔS^o(J.mol^{-1}.K^{-1})
With varnish	62.21	125.18
Without varnish (acetone)	72.93	154.15
Without varnish (acetone + sanded)	127.49	364.60

Statistical analysis

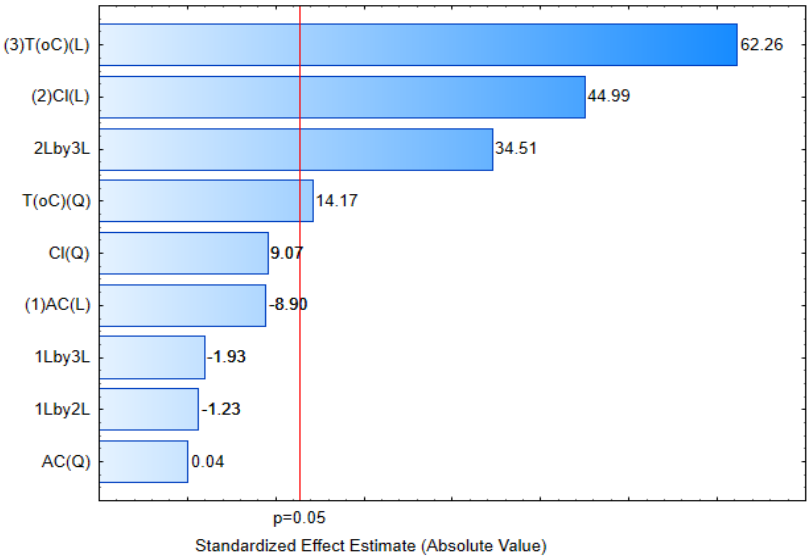
The Pareto diagram, Figure 6, shows the results of the effects of the variables chloride concentration, citric acid concentration and temperature on the corrosion rate of packaging samples with and without varnish, considering their linear and quadratic terms, as well as the interaction between the variables.

It can be seen that, in both cases, temperature and chloride concentration have a significant effect on the corrosion rate at the 5% significance level ($p < 0.05$), with temperature being the most influential factor. It can be seen that the samples with varnish had effects of a lower magnitude when compared to the packaging without varnish, which shows the efficiency of the protective layer on the packaging studied.

Figure 7a shows that the corrosion rate is strongly influenced by high temperatures and high chloride concentrations for the varnished sample. On the other hand, the lowest CR values are obtained at lower temperatures and low chloride concentrations. In the analysis of the sample with varnish, for the concentration of chloride close to that obtained in the soft drink analyzed (0.17 g/L), CR is significantly influenced by the variable studied only for temperatures above 45 ^{o}C, as shown in figure 7a. For the sample without varnish, it can be seen that the corrosion rate in these packages is more significant when compared to the packages with varnish. Temperature and chloride concentration are more significant when both variables are high, the red region shown in figure 7b.

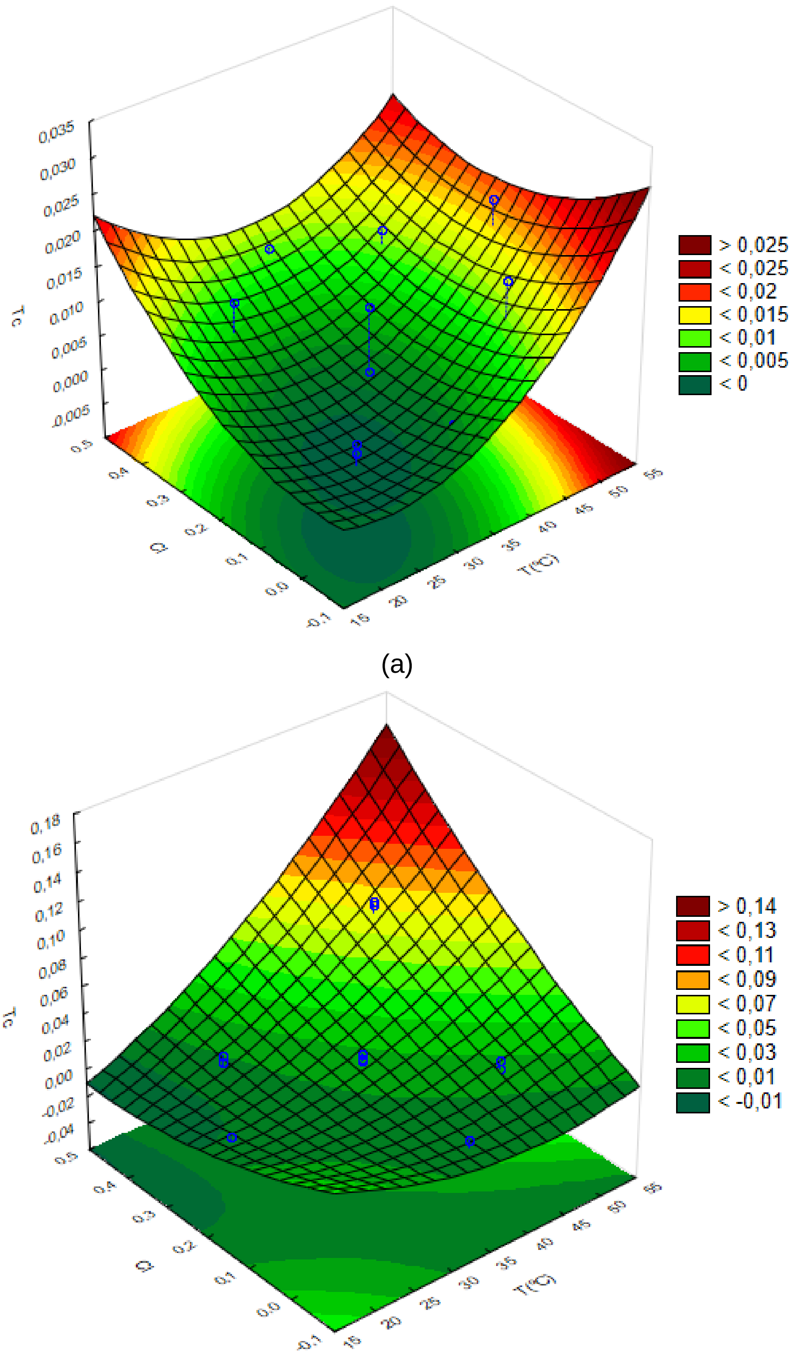


(a)



(b)

Figure 6. Effect of temperature, chloride concentration, citric acid and their interactions on the corrosion rate of samples (a) with varnish and (b) without varnish. *CA: citric acid.



(a)

(b)

Figure 7. Response surface for the corrosion rate variable as a function of chloride concentration and temperature (a) with varnish and (b) without varnish.

Conclusion

In this study, it were characterized cola soft drinks and their interaction with aluminum packaging under different conditions. As for the characterization of the drink, the values obtained were pH =2.5; 7.5 ºBrix; chloride concentration of 0.17g/L, acidity 0.17 %m/m; density 1.04 g/mL and concentration of reducing sugars 11.3 %m/m.

The electrochemical measurements, via linear polarization, and the statistical analysis showed that for the unvarnished sample with a chloride concentration that was close to that of the beverage (0.17 g/L), the CR was more significant at temperatures above 45°C. For the sample without varnish, CR was more significant when both temperature and Cl- were high.

The protective effect of the varnish was also shown by the activation energy of the corrosion process, where the sample without varnish had a lower value (AE = 67.48 kJ/mol) than the sample with varnish (AE = 88.92 kJ/mol). The ΔHº and ΔGº activation parameters of the process were positive, showing that the corrosion process is endothermic with an increase in disorder with the removal of the varnish.

In this study, the packaging proved to be safe from corrosive processes due to its protective varnish layer, thus preserving the quality of the product.

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