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Characterization of Carbonated Beverages Associated to Corrosion of Aluminium Packaging

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The objectives of this study were to evaluate the characteristics of commercial soft drinks related with the corrosion process of the aluminium packaging and based on that, propose model solutions for future studies of beverage/package interaction and corrosion process of metal packages. Therefore, the pH, acidity, concentration of chlorides and copper in six types of soft drinks were determined, as well as the corrosion potential of the aluminium and the current density corrosion obtained in polarization curves using the beverages as electrolyte. Based on the results obtained, a solution of citric acid (pH = 3) containing chloride (250 mg/kg) and copper ions (250 μg/kg) is proposed. The obtained results are potentially useful for the industry and future studies regarding the interaction process between soft drinks and aluminium cans. Copyright © 2016 John Wiley & Sons, Ltd.

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INTRODUCTION

Metal packages are widely used for packaging food, with the advantages of high mechanical strength, toughness and impermeability. However, the key limitation to their use concerns interactions between the package and the foodstuffs, such as corrosion and the migration of metals to the products.[1]

Corrosion is the result of physical and/or chemical interactions between the material and the environment to which the material is exposed. Internal corrosion of metal packages in contact with food and beverages cause two considerable factors: migration of metals from the package to the food and loss of quality and integrity of the processed products, resulting in economic impacts to the food industry. The migration of metals from the package to the food can render it unfit for consumption if the concentration of metal is higher than the tolerated limits, as well as causing undesirable reactions to the product, such as colour change and the catalysis of oxidizing processes, among others.

The main factors that influence the rate of metal corrosion are the dissolved oxygen (directly related with the air/oxygen content inside the package), pH and composition (as the dissolved salts, ions and molecules) of the product and the environment conditions (such as the temperature). The oxygen, as well as the dissolved ions, can accelerate corrosion because of their depolarizing action.

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In aluminium alloys, the corrosion process is facilitated by the contact with less electronegative elements, such as copper (Cu^{++}) and chlorine (Cl^{-}). Some other food constituents, such as pigments and metallic ions, are also corrosion promoters,[2] highlighting the importance of evaluating the related beverages.

The oxide film formed, as a result of the combination of aluminium with the oxygen (Al_2O_3 and $Al_2O_3.H_2O$) on the material surface, is unstable in pH lower than 4.5. This is the pH condition of various beverages such as soft drinks and juices, which present a favourable medium for corrosion development. The solubility of this film exposes the surface of the material to corrosive processes that can be accelerated by the presence of catalyzers ions (i.e. Cl^{-}, Cu^{++}), the oxygen in the environment and the residues of sanitizers.[2,3] Consequently, the importance of evaluating those properties on commercial beverages is highlighted.

The Brazilian and European legislation[4,5] establishes the use of 3% acetic acid as an acidic food simulant ($pH < 4.5$) to assess the adequacy of polymeric materials, which will be in contact with foodstuff. However, the acetic acid is not used in the beverage formulations because of its unpleasant sensorial perception, and it has proved to be very aggressive to metal packages. Consequently, its use as beverage simulant certainly would result in an inappropriate conclusion for corrosion studies, highlighting the need for establishing appropriated simulants.

The objectives of this study were to evaluate and compile the information on different commercial soft drinks related with the corrosion process of drawn and wall ironed aluminium cans, and based on that, propose model solutions for future studies of beverage/package interaction and corrosion process of metal packages.

METHODOLOGY

Material

The following types of soft drinks were analysed: tonic water, cola, orange, lemon, guaraná and grape. The samples of commercial brands prevailing in the Brazilian market were acquired in supermarkets in Campinas, São Paulo, Brazil, packed in 350 ml aluminium cans. All cans of the same beverage belonged to the same production lot, based on information provided by the producer.

The samples were evaluated for their pH, acidity, concentration of chlorides and copper, determination of the gaseous volume inside package and the aluminium corrosion potential. All the evaluations were carried out with five replications in an atmosphere conditioned at a temperature of 23°C.

Determination of the pH and acidity

The pH was directly determined in beverages before their decarbonation using a pHmeter model B474 (Micronal, São Paulo, Brazil) that was also utilized for acidity determination. To determine acidity, 10 g of the sample previously decarbonated were weighed on an analytical scale model AT 201 (Toledo Mettler, Greifensee, Switzerland) and then transferred to a 125 ml Erlenmeyer containing 50 ml of ultrapurified water. Titration proceeded with the use of 0.1 M sodium hydroxide solution up to 8.1 pH.[6]

Concentration of chlorides and copper

The concentration of chlorides was determined by volumetric analysis (titration).[6] An aliquot of 20 g of the sample was weighed in platinum capsules, previously cleaned and washed with nitric acid and with ultrapurified water and evaporated on a heating plate. They were then incinerated in a muffle furnace heated by a microwave model Pyro touch control (Milleston, Sorisole, Italy) at a temperature of 550°C until ashes were obtained. The ashes were solubilized in ultrapurified water and transferred to 100 ml volumetric flasks. The pH of the solutions was adjusted to 6.5–9.0 with sodium hydroxide.

Finally, an aliquot of 10 ml was titrated with a solution of silver nitrate (0.005 M), after the addition of 10% potassium chromate as indicator, until the appearance of a reddish precipitate in the solution. The result was expressed in percentage of chloride.

The concentration of copper in the beverages was determined by direct measurement of a solution containing 22.5 ml of previously decarbonated beverage, acidified in 2.5 ml of concentrated nitric acid P.A., through an inductively coupled plasma optic emission spectrometer (ICP OES, model OPTIMA 2000 DV, PerkinElmer, Waltham, USA) using appropriate calibration curves.

Determination of the gaseous volume

The evaluation of the volume of carbon dioxide (CO_2) present in the aluminium cans of carbonated beverages was carried out following standard ASTM F1115-95.[7] Therefore, it was used an air analyser instrument (model 'New Style', Zahm and Nagel Co., Holland, USA) and a 25 ml volumetric burette, with the objective of determining the CO_2 and the other gases content present in the can separately. After the manometric determination of the CO_2 concentration, expressed in volumes of CO_2/volume of water, was completed as per ASTM F 1115-95,[7] the residual gaseous volume was determined by means of the reaction of the gases present in the interior of the package with a 30% sodium hydroxide aqueous solution, which reacts with the CO_2, forming water and sodium carbonate. This way, as CO_2 has been consumed, the residual volume is composed of gases other than CO_2.[8]

Determination of the corrosive potential of aluminium

The measurements were performed in triplicate using a potentiostat/galvanostat EG&G model 273A system (Princeton Applied Research, Oak Ridge, USA), operating with the EG&G52 software (Princeton Applied Research, Oak Ridge, USA), and an electrochemical cell with a three-electrodes arrangement. The potential measurements were recorded with respect to the saturated calomel electrode as reference and platinum as counter electrode.

The aluminium sample of 19.6 cm^2 was used as work electrode, while the beverage was used as electrolytic solution. The aluminium sample was collected from the body wall of cans, whose varnish coat was previously removed with solvent (acetone P.A.), followed by polishing with 600 grade emery paper and rinsing with ultrapure water. The soft drink samples were previously de-carbonated and deaerated through agitation and bubbling with ultrapure nitrogen. The open circuit potential (OCP) of the aluminium in the beverage were monitored for 1 h to achieve the stationary state.

Based on the aluminium OCP information, a potentiodynamic method was used, consisting of the application of small increments at the system potential and recording the current response. For this purpose, a scan rate of 1 mV/s, in the potential range of −400 mV (cathodic curve) up to +400 mV (anodic curve), with respect to the corrosion potential was applied. The current response was measured as a function of the potential applied. It resulted in plots of the potential (E) versus the logarithm of the corrosion current density (log (j)).

The kinetic parameters of the corrosion process were determined from the polarization curves obtained for each one of the beverages, utilizing the Parcalc analysis module, from the EG&G52 software. The density of the current (j_{corr}) was determined from the extrapolation of the Tafel region (linear part of the cathodic polarization curve) up to the intersection with the corrosion potential (E_{corr}). The linear portion of the polarization curve was selected from an overpotential (η) of ±50 mV, in relation to the E_{corr}.

RESULTS AND DISCUSSION

Determination of pH and acidity

The results of the pH and acidity determinations in the beverage samples are shown in Table 1. The acidity was expressed as citric or tartaric acid, according to the type of beverage and Brazilian legislation.[9]

The cola soft drink was the beverage with the lowest pH (2.49) and the lowest acidity (0.081%). It is a consequence of the acidulant used in its composition, the phosphoric acid (INS 338), while the other beverages use the citric acid. According to Brazilian Directive no. 544/1998,[9] which lays down the

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Table 1. Results of pH and acidity for the six samples of soft drinks (mean of five replicates ± standard deviation).

Sample	pH	Acidity (%, expressed in m/m)
Tonic water[1]	2.93 ± 0.08	0.193 ± 0.005
Cola soft drink[1]	2.49 ± 0.04	0.081 ± 0.013
Lemon soft drink[1]	3.25 ± 0.01	0.138 ± 0.001
Orange soft drink[1]	3.68 ± 0.02	0.175 ± 0.005
Guaraná soft drink[1]	3.32 ± 0.01	0.106 ± 0.002
Grape soft drink[2]	3.44 ± 0.01	0.160 ± 0.001

[1] Corresponding acid: citric;
[2] Corresponding acid: tartaric.

standards for the identity and quality of soft drinks, the titratable acidity in cola soft drinks should be expressed in citric acid, as shown in Table 1.

Among the beverages that are acidified with organic acids, tonic water is the soft drink with the lowest pH (2.93) and the highest acidity (0.193%). The Brazilian legislation[9] lays down the minimum acidity values for the beverages assessed in this study, with the exception of tonic water, for which a reference value is not defined. For the other beverages, the values shown in Table 1 comply with this legislation.

The observed acidities indicate that the evaluated beverages are favourable medium for the development of aluminium corrosion.[10] Organic acids present in food, such as citric and tartaric acids, are substances that promote the anodic corrosion of metals, as they favour the migration of metallic ions to the aqueous phase.[2] Therefore, it is an important parameter in the studies on corrosion of metal packages for food and beverages to characterize the type and concentration of these acids.

The results shown in Table 1 demonstrate that all the studied beverages presented critical values of pH for aluminium, i.e. values that are favourable to the development of corrosion in this metal ($pH < 4.5$). Further, it serves as a base for the definition of model solutions for the study of corrosion in metal packaging for soft drinks. Hence, the results show that for beverages acidified with citric acid, a model solution pH of 3.0 can be defined, while for beverages based on phosphoric acid the pH of 2.5 should be defined. In each case, the respective acids should be used in the preparation.

Concentration of chlorides and copper

The concentrations of copper and chlorides in carbonated beverages are shown in Table 2.

The evaluated beverages exhibited very low concentration of copper in their composition. Only the orange and the grape soft drinks showed values over the quantification limit (QL) of the method in the analytical conditions used. The orange soft drink showed a concentration of copper of 17.89 ± 1.91 μg/kg, being 225.16 ± 10.84 μg/kg for the grape beverage. The other beverages (tonic water, cola soft drink, lemon soft drink and guarana soft drink) presented values lower than the method's QL, which was 4.0 μg/kg. The current Brazilian legislation establishes that the contents of copper

Table 2. Concentration of chlorides, expressed in mg/kg, and of copper in μg/kg for the six samples of soft drinks (mean of five replicates ± standard deviation).

Sample	Chlorides (mg/kg)	Copper (μg/kg)
Tonic water	247.6 ± 99.9	≤4.0*
Cola soft drink	102.3 ± 18.1	≤4.0*
Lemon soft drink	146.5 ± 36.0	≤4.0*
Orange soft drink	120.1 ± 15.1	17.89 ± 1.91
Guaraná soft drink	134.0 ± 18.3	≤4.0 *
Grape soft drink	110.5 ± 32.5	225.16 ± 10.84

*Quantification limit of the method in the analytical conditions used.

in the soft drinks cannot exceed 5000 μg/kg. For comparison, according to the Codex Alimentarium,[11] the maximum Cu value for mineral water is 1000 μg/kg. Therefore, the observed values can be considered adequate.

Rizzon and Link[12] evaluated the composition of homemade grape juice from different varieties of crops and quantified copper between 1.3 and 4.5 mg/kg, according to the variety analysed. Therefore, the contents of copper in the grape soft drink are probably due to the use of natural juice in the formulation of this beverage (as attested by its composition) and probably due to the products used on the grape production.

The results for quantification of chlorides were very close to those of all the beverages. This is a very important finding, as the aggressive chloride ion (Cl^-) is the main cause of pitting corrosion.

It is known that the corrosion in metallic materials proceeds more rapidly in substrates with small defects in the polymeric layer because of the high energy involved in the corrosion process, which is concentrated at the region with defect. Metallic packages can be internally coated with several different varnishes, which have different properties and show different behaviours during storage of foodstuffs. Therefore, the can manufacturing may affect the integrity of the varnish, especially when the coating is applied prior to material casting.[8] However, the aluminium cans are usually coated with epoxy-acrylate resin-based lacquer, and this step occurs after the formation of the body by the draw and wall ironing process.[13,14] Although the polymeric layer is added in order to avoid the food–package interaction, and it should be continuously and perfectly fitted to the metal surface, small points of imperfections/discontinuities may appear as a consequence of an inappropriate coating condition. Therefore, interactions between the food/beverage and the package may happen at these points, and the corrosion process can be initiated thereon. In fact, the metal exposure is a critical control point in the can manufacturing, being the production occasionally lost because of the beverage–metal contact and interaction.

Further, Fontana[15] suggests that because they are extremely small, the chloride ions can diffuse through the film of oxides, being available for reactions with the surface of the metallic material. According to Halambek *et al.*,[16] the chloride ions lead to initiation and growth of corrosion pits in aluminium alloys, as a result of the localized breakdown of the passive film.

The results obtained, therefore, highlight the need for guarantee a good coating for the aluminium packages in the evaluated products.

The Brazilian legislation[9] does not impose any restrictions to the presence of chlorides and copper in beverages. For comparison purposes, the Brazilian legislation for water for human consumption[17] considers that the maximum limit of chlorides allowable in potable water is 250 mg/kg.

The results obtained indicate that most of the beverages show a similar concentration of chlorides (the overall mean of soft drinks was 143 mg/kg), being that tonic water exhibited a mean value of 247.6 mg/kg, i.e. very close to the limit established for potable water. Chloride is usually found in processed food and beverage, because of the use of its salts during the processing of foodstuffs. In beverages such as soft drinks, its major source is the water, because other ingredients do not intentionally contribute to the amount of chloride. It is also an essential nutrient and can be found in sport drinks because of the use of calcium chloride and magnesium chloride as electrolyte.

Determination of the volume of gas

The gas volume was determined in beverages packed in 350 ml aluminium cans. The results shown in Table 3 indicate that there is no standard for the quantity of volume of gas (excluding CO_2) in the commercial cans, as this quantity varied greatly among the samples analysed. Furthermore, the orange soft drink showed one package with 25 ml of gas and another can with a greater value, which could not be quantified because of the maximum measuring limit of the system used in this study (25 ml).

The volume of carbonation of the beverages, expressed as volume of carbon dioxide (CO_2) per volume of water[7] at a temperature of 23°C, exhibited values compatible with those applied by soft drink manufacturers, i.e. in the order of 2.5 to 4 volumes of CO_2/volume of water, depending on the type of beverage,[18] the formulation and the amount of sugar (°Brix).

Table 3. Quantification of gaseous volume (at 25°C and atmospheric pressure) and carbonation volume for the six samples of soft drinks (mean of five replicates ± standard deviation).

Sample	Gaseous volume (ml)	Carbonation volume*
Tonic water	20.1 ± 0.4	3.44 ± 0.09
Cola soft drink	11.3 ± 3.5	3.74 ± 0.09
Lemon soft drink	9.8 ± 4.0	3.57 ± 0.08
Orange soft drink	>21.9 ± 2.3	3.23 ± 0.08
Guaraná soft drink	5.6 ± 2.5	3.58 ± 0.05
Grape soft drink	19.1 ± 2.0	3.53 ± 0.11

*Volumes of CO_2/volume of water at 23°C.

The variation in the quantity of gas inside the packages of the samples analysed shows that there are no general criteria established or practised by the beverage industry to control this parameter, although this is an important criterion when considering the metal corrosion.

According to information provided by packaging industry, it is normal to occur an unsuitable injection of nitrogen during the filling and seaming step in the soft drink line production, because of erroneous adjustment or even not properly operation of the machine. The presence of oxygen (from the air) in the package can accelerate the corrosion process, as well as high quantity of air in the container headspace can contribute to the presence of oxygen.

Determination of the corrosive potential of aluminium

The results of the potentiodynamic polarization curves are shown in Table 4. Figure 1 shows an example of the polarization curve obtained for the soft drinks analysed, once all the drinks presented the same curve profile. The analysis of the polarization curves demonstrated that the anodic and cathodic portions were not similar. According to Seruga and Hasenay,[19] this indicates that the corrosive process does not consist of the simple dissolution of aluminium and the release of hydrogen (H_2) and that other parallel reactions occur.

Lower values of corrosion potential (E_{corr}) indicate greater activity in corrosion of the material. In general, lower values of E_{corr} are associated with larger concentrations of acids. However, when the values of E_{corr} were compared with the acidity in the analysed beverages, this association could not be made. The beverage with the lowest E_{corr} (cola soft drink) was the one with the lowest concentration of acid (Table 1). Another parameter that indicated the interaction of the beverage with the metallic material is the density of the corrosion current (j_{corr}). The higher its value, the faster the corrosion rate will be. In this manner, the cola soft drink is once more identified as being the most critical one. It is necessary to highlight that, although its concentration of acid is lower, the cola soft drink is acidified with phosphoric acid (H_3PO_4), which is a trivalent inorganic acid, on contrary of the other beverages (acidified with citric acid). It also highlights that the model solutions must be prepared with the same acid of the simulated beverage.

Although the cola soft drink appears to be more aggressive to the metallic material than the other soft drinks evaluated, it is important to point out that most of these foods and beverages are acidified

Table 4. Kinetic parameters of corrosion determined in the beverages in relation to the material of the body of the package (mean of five replicates ± standard deviation).

Sample	E_{corr} (V)	j_{corr} (10^{-6}A.cm^{-2})
Tonic water	−0.563 ± 0.002	43.19 ± 16.01
Cola soft drink	−0.742 ± 0.014	85.17 ± 1.67
Lemon soft drink	−0.578 ± 0.017	22.48 ± 13.94
Orange soft drink	−0.578 ± 0.011	0.682 ± 0.164
Guaraná soft drink	−0.642 ± 0.019	1.594 ± 0.241
Grape soft drink	−0.539 ± 0.057	15.43 ± 5.08

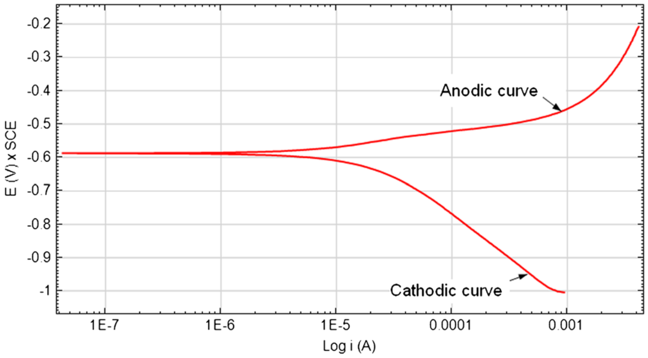

Figure 1. Polarization curve measured for aluminium alloy AA 3104 in soft drinks.

with citric acid. Therefore, it is not possible to discard the use of this acid in the studies of the interaction between food and package.

Among the soft drinks acidified with citric acid, tonic water is the beverage with the highest concentration of acid and the lowest pH. Correlating these parameters with the results obtained in the polarization curves, it can also be seen that the j_{corr} is higher for tonic water in relation to the other beverages acidified with citric acid. However, with regard to the corrosion potential, the tonic soft drink did not show higher values compared with the other studied beverages. In tonic water soft drink, a larger concentration of chlorides was found in comparison with the other studied beverages. The evaluation of all the studied parameters collaborates to pointing this soft drink as being the most critical to the aluminium package, among the soft drinks acidified with citric acid.

In general, these results show that decreasing pH shifts the j_{corr} to higher values. It is in accordance with the findings reported by Mayouf *et al.*[20] It is important to highlight the low range of pH for the beverages analysed ($\Delta pH = 1.19$), which results in great difference for j_{corr} measured among the different beverages studied. It is known that lower pH of the media allows the aluminium oxide layer dissolution and therefore influences the corrosive behaviour of the material.

The presence of chloride in the solution and its influence in the aluminium corrosion are well discussed in literature, although the mechanism of Cl^- ions penetration in the oxide layer is not completely known.[21] Considering the citric-based drinks, higher values of j_{corr} are observed for beverages with upper content of chloride. These experimental observations are in accordance with literature, linking the influence of pH and chloride concentration in the aluminium alloy AA3104 corrosion density current and considering beverage products.

Although the grape soft drink analysed had shown the lowest chloride concentration, the j_{corr} measured for the material studied is not the lowest one. Moreover, the corrosion potential measured after the aluminium contact with this soft drink was the highest one. It occurs due to the presence of copper ions in the beverage. Bakos and Szabó[22] observed the cementation of copper ions on aluminium surface, creating an Al-Cu bimetallic system and, after a while, beginning the pitting corrosion. This deposition shifted the corrosion potential in the positive direction. Thus, the experimental observation using soft drinks is in good agreement with the mentioned study.[22]

The orange soft drink has higher acidity compared with the lemon soft drinks, being expected a more negative E_{corr} value of aluminium when it is in contact with the orange beverage. Nevertheless, the orange drink has copper in solution, which certainly contributes to the increasing of E_{corr}, because the copper's reduction potential is high ($Eo = +0.340\,V - Cu^{2+} + 2e^- \rightarrow Cu$) and shifts the E_{corr} to higher values.

Figure 2 compiles the j_{corr}, chloride and copper ions concentration data for all analysed beverages. The results were organized from lower to upper values of pH. Looking to the citric-based soft drinks results, it can be stated that increasing the pH and decreasing the chloride concentration, lower values of j_{corr} will be attained, indicating less corrosion velocity of the metallic material. The influence of the copper on the grape soft drink is also easily observed in this figure.

Concerning the cola-based soft drink, its aggressivity is evident, even when relative low value of chloride and copper ions is present in solution. Therefore, the low pH and the kind of acidulant are

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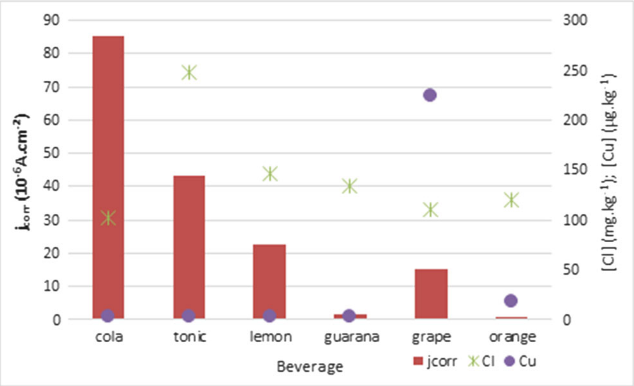

Figure 2. Comparison data: j_{corr} versus ions concentration. Data ordered from lower to upper value of pH.

very important parameters on the influence of aluminium corrosion and consequently should be considered in the definition of a model solution to be employed in corrosion studies.

Hence, the use of a solution with citric acid at pH = 3.0, chloride ion concentration of 250 mg/kg and copper ion concentration of 250 µg/kg is very appropriate to be employed in corrosion studies aiming to the development and the improvement of aluminium cans for soft drinks. The use of phosphoric acid for metal cans designed for cola-based soft drinks is also recommended.

Organic acids release hydrogen to the environment until they reach equilibrium. Table 5 shows the pKa values of citric, phosphoric and tartaric acids in the beverages analysed.[23] The pH of all the beverages (Table 1) is close to the pKa_1 of the corresponding acids, indicating that approximately half of the molecules present have only one of their groups dissociated. Therefore, the non-dissociated form is the most abundant in the medium.

Citric acid, for example, is a tricarboxylic acid; the acidity of which is due to three carboxyl groups (-COOH), which can lose one proton in solutions. Consequently, a citrate ion is formed in the aqueous medium. Citrates are good controllers of pH of acid solutions. Furthermore, they are metal chelators, which can favour the metal dissolution process of the package into the product. It is important to mention that other substances in the beverage, further than acids, can also affect the complexes formation and the corrosion parameters of the metallic package (juice components, as tannins or anthocyanins; additives, such as the preservatives, etc.).

CONCLUSIONS

The present work evaluated the six main soft drinks of the Brazilian market in relation to the properties that affect the corrosion of aluminium cans. Based on the obtained corrosion potential (E_{corr}) and current density of corrosion (j_{corr}), the cola-based soft drink was the most aggressive beverage to the corrosion of aluminium, followed by the tonic water. These two beverages also showed the lowest pH values. The highest concentration of chloride, an aggressive element to the aluminium corrosion process, was also determined in the tonic water. The presence of copper, an important element with respect to the aluminium corrosion, was determined at low concentration in grape and orange soft drinks and was attributed to the use of natural juice in the beverage formulation.

Table 5. pKa of acids present in the beverages analysed (Atkins and Paula, 2011).[23]

Acid	pKa_1	pKa_2	pKa_3
Citric ($C_6H_8O_7$)	3.15	4.77	6.40
Phosphoric (H_3PO_4)	2.12	7.21	12.67
Tartaric ($C_2H_4O_2(COOH)_2$)	3.22	4.82	—

The obtained results are potentially useful for the industry and for future studies regarding the interaction process between food and packages. Based on these results, we would suggest the use of model solutions to evaluate the behaviour of metallic packages regarding the interaction with beverages. Based on these results, we conclude that the behaviour of metallic packages regarding the interaction with beverages would be successfully evaluated by the use of an aqueous solution of citric acid pH 3.0, with chloride concentration of 250 mg/kg and copper concentration of 250 µg/kg, considering soft drinks in general. For phosphoric acid-based soft drinks, we recommend to adjust the aqueous solution using phosphoric acid and pH 2.5 to suit the model solution as the real beverage.

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