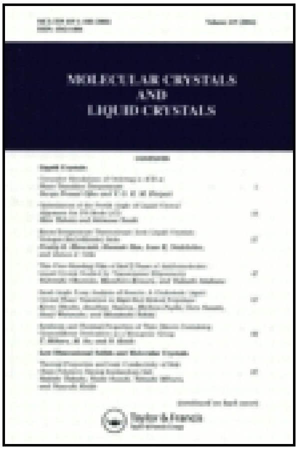

Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

PAni as Prospective Replacement of Chromium Conversion Coating in the Protection of Steels and Aluminum Alloys

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To cite this article: D. Huerta-Vilca, B. Siefert, S. R. Moraes, M. F. Pantoja & A. J. Motheo (2004): PAni as Prospective Replacement of Chromium Conversion Coating in the Protection of Steels and Aluminum Alloys, Molecular Crystals and Liquid Crystals, 415:1, 229-238

To link to this article: http://dx.doi.org/10.1080/15421400490482213

Mol. Cryst. Liq. Cryst., Vol. 415, pp. 229–238, 2004
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ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421400490482213

PANI AS PROSPECTIVE REPLACEMENT OF CHROMIUM CONVERSION COATING IN THE PROTECTION OF STEELS AND ALUMINUM ALLOYS

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Corrosion inhibition properties of chemical and electrochemically synthesized polyaniline (PAni), poly-o-methoxianiline (POMA) and their copolymers, in form of coatings of stainless steel AISI 304 and aluminum alloy 6061-T6 are studied in 3% and 0.1 M NaCl solutions, respectively. Polarization curves showed that the protection of steels by PAni is of anodic nature by setting the redox potential in the passive potential of the substrate. However, the protection of aluminum alloys after separation of both the corrosion and pitting potential is also anodic.

Keywords: AA6061-T6; AISI 304; copolymers; corrosion protection; PAni; POMA

INTRODUCTION

DeBerry [1] found in 1985 that PAni-coatings ennoble the corrosion potential of stainless steel AISI 430 in 1 M H_2SO_4. Since then, many research groups have been interested in the study of PAni for corrosion inhibition of mild and galvanized steels [2–6]. Chromate conversion coatings have been classified as toxic and carcinogenic since the 1970s [7]. Therefore, the replacement of such coatings by environmentally and non-toxic coatings is justified.

Racicot *et al.* [8] covered the aluminum alloy 7075-T6 by a double strand of PAni and a polyanion and tested in 0.5 M NaCl. They found that the conducting

The financial support of FAPESP (Processes 99/11621-7 and 00/02674-9) is gratefully acknowledged.

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polymer-coating decreases the corrosion current two orders of magnitude over the uncoated alloy and one order over the non-conducting form.

In recent years, the corrosion tests performed on PAni-coated aluminum alloy 2024-T3, which is used in aircraft, gave enormous ennoblement of the corrosion potential [9]. Corrosion protection coatings are long-term applications (ca. 30 years durability in military aircraft) [10], thus the stability of the redox potential of polyaniline and their derivatives should be guaranteed. The insolubility of PAni in common solvents constitutes a drawback to the applications. Efforts in plastifying by ring- or N-substitution with sulphonic groups have produced positive effects. Copolymerization leading to soft polyaniline is another alternative to enhance its processability [11–13]. The protection of steels by PAni is of anodic nature by setting the redox potential in the passive potential of the substrate [14,15]. On the other hand, the protection of aluminum alloys after separation of the corrosion potential to negative values where no pitting corrosion occurs is also anodic [16].

In the present study, homo- and copolymers of PAni and poly (o-methoxianiline) (POMA) were synthesized and their corrosion protection properties as coatings of stainless steel AISI 304 and aluminum alloy 6061-T6 were investigated. Particular attention was paid to the advantage of copolymers in relation to homopolymers.

2. EXPERIMENTAL

Aniline and o-anisidine (also called o-methoxianiline) were cleaned from oxidation impurities by distillation over zinc dust at 150°C. The copolymers (aniline-co-o-methoxianiline), were synthesised in 1 M HCl solution containing 0.1 M of monomers in different ratios. The chemical oxidative polymerisations were performed through dropwise addition of 0.1 M ammonium persulphate under constant stirring. Homopolymers were prepared from either 0.1 M aniline or 0.1 M o-anisidine in 1 M HCl solution, respectively. The reaction bath and the oxidation agent in a separate burette were maintained at 0°C. The polymerisations were monitored by recording temperature and potential for around 2 hours. After this reaction time, the mixture of polymer containing rest of electrolyte was filtered, washed repeatedly with 1 M HCl solution and distilled water until a colourless washing solution was obtained. The remaining polymer material in its conductive form was dried in a heater at 40°C for 2 hours, undoped in 0.1 M NH_4OH for 20 hours under stirring, until pH of around 10 was attained. The undoped polymer in ammonium hydroxide was filtered, washed with distilled water and dried under dynamic vacuum at 60°C, and finally conserved in vacuum until analysis.

The as-obtained polymers were submitted to crystalline structure studies by X-ray diffraction (XRD) with Cu Kα radiation at θ-2θ mode. The apparent grain size of the polymers was estimated from the full width at half maximum (FWHM) of the most intense reflection according to Scherrer's equation, $t = 0.9\ \lambda/B \cos\theta$, where t is the apparent grain size, λ is the X-ray wavelength (0.15418 nm for Cu Kα), B is the FWHM in radian and θ is the diffraction angle.

The corrosion protection property of polymer coatings on stainless steel AISI 304 and AA6061-T6 were studied in $0.5 \leq pH \leq 5.76$ and 0.01 M NaCl (pH = 6.02) solutions, respectively, at 23°C. Before coating, the substrate disks of 1 cm^2 surface area were machined and degreased in acetone and ultrasound. An electrical connection lead of Pt-wire was spot-welded on the backside of the disks. The samples were then embedded in acrylic resin leaving part of the wire free. After polishing in emery paper (320-1200 grade), degreasing in ethanol and drying at 40°C, the specimens of AISI 304 were immediately electrocoated in the respective monomer solutions used for co- and homopolymerisation. Homo- and copolymers were drop-casted on aluminium alloy 6061-T6 with paints prepared of 0.8% of emeraldine base (EB) powder in NMP. Their emeraldine salt forms (ES) were obtained by exposing them 20 hours to the vapour of 1 M HCl.

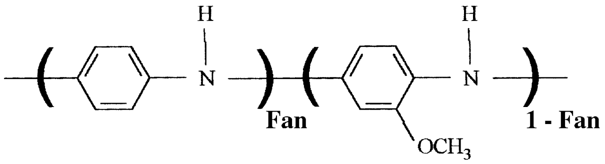
A single compartment electrochemical cell, with a platinum foil (2 cm × 2 cm) counter electrode and a saturated calomel electrode (SCE) reference electrode, was used. The polarization curves as well as cyclic voltammograms were measured on a potentiostat/galvanostat (EG&G PARC model 273 A), by using the softwares M352 and M270, respectively.

Adherence of polymers to the substrate were tested by Sellotape-test which consisted of applying with a thumbnail pressure over the entire surface area, which was removed by slow peeling with pulling back of the tape. The remaining underlying surface of polyaniline after each removal was characterised by cycling the electrode in monomer-free electrolyte. Films were considered to have good adherence when they remained intact after two operations.

RESULTS AND DISCUSSION

Copolymer Structure

A general formula of the copolymer poly (ani-co-o-methoxianiline) is represented as



where Fan is the molar fraction of aniline units and $0 \leq Fan \leq 1$.

Film Preparation and Characterization

Figure 1 shows typical cyclic voltammograms (CV's) recorded during the deposition of homopolymers and the copolymer 1:1. In the CV′s of PAni (Fig. 1a), peaks I_a, II_a and III_a accompanied by their respective reduction peaks I_c, II_c and III_c describe the polaron, bipolaron and degradation by hydrolysis, respectively. In POMA (Fig. 1b), the peak III_a just appearing in the first cycle corresponds to an additional oxidation process, but not to hydrolysis. It is important to note that the oxidation process (Ia) is responded by three reduction peaks I'_c, I''_c and III'''_c which describe step-wise reduction processes. The CV's of the copolymer 1:1 (Fig. 1c) resemble that of POMA, with the small difference that the autocatalytic current rises are better observed in this low current scale. From the first oxidation peak, it can be stated that homopolymers grow faster than copolymers.

Structure analysis by XRD showed that POMA is amorphous, while PAni is crystalline, and the copolymer 50:50 presents a crystallinity between the corresponding to the homopolymers. The apparent grain sizes estimated from the FWHM are 0.165 nm for the POMA, 0.424 nm for the copolymer 50:50 and 1.129 nm for the PAni.

Corrosion Protection

a) Stainless Steel AISI 304

AISI 304 is an 18/8 chromium-nickel austenitic stainless steel widely used in the industry (chemical, pharmaceutical, textile, petro-chemical and cellulose). It shows resistance to organic acids, but is prone to pitting.

The corrosion protection of steels by PAni can be evaluated in terms of corrosion potential (V_{OC}) shifts to more noble values in comparison to that of the bare steel. PAni in doped form on AISI 304 shifts the V_{OC} from -0.290 to -0.190 V *vs.* SCE. The doped copolymer 50:50 with POMA shifts to $+0.090$ V. This indicates that a copolymer coating offers a greater corrosion protection than pure polymers.

Dedoping of the copolymer in NH_4OH solution promotes not only an additional ennoblement of around $+0.040$ V but the corrosion rate decreases by one order of magnitude. These open circuit potentials (OCPs) of the polymer-coated electrodes are situated in the passive region of the uncoated AISI 304. Consequently, the coatings offer anodic protections to the substrate.

b) Aluminum Alloy 6061-T6

Aluminum alloy 6061-T6 (AlMgSi1) contains 0.8–1.2% Mg and 0.4–0.8% Si, and is employed after heat treatment T6 (solution heat treated, artificially aged). PAni, POMA and their copolymers were tested

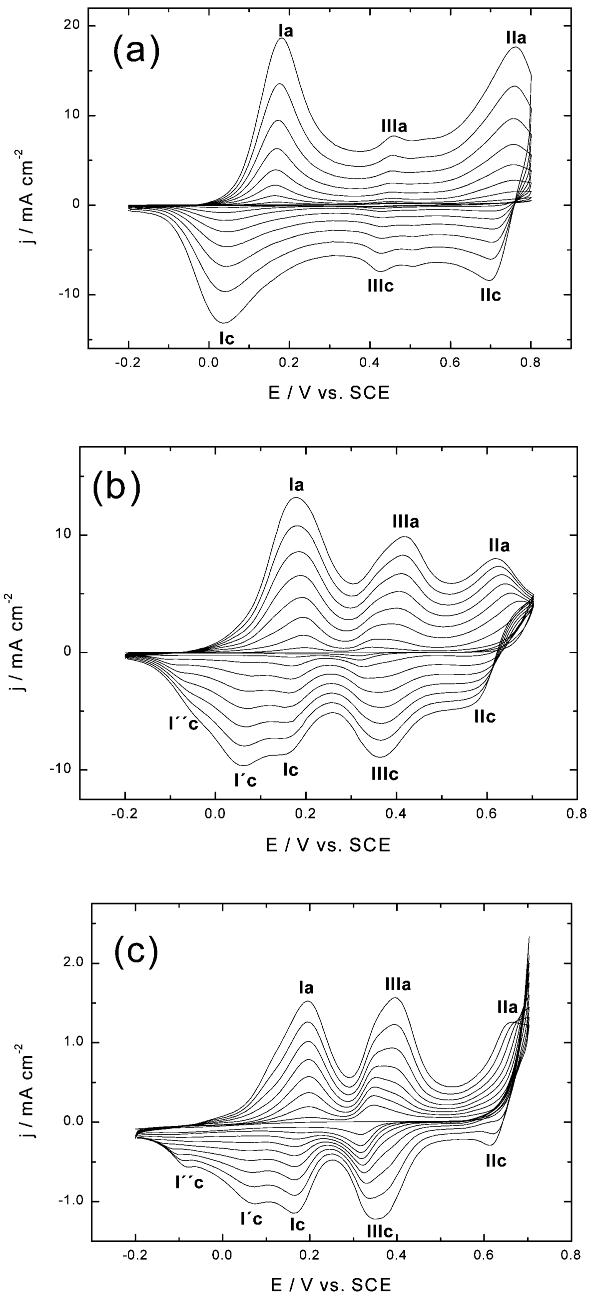


FIGURE 1 Cyclic voltammograms for the synthesis of polymer films from 0.1 M aniline and (x/0.1)M o-methoxianiline in 1 M HCl solutions, between –0.2 and +0.8 V *vs.* SCE at 50 mV sec^{-1}.

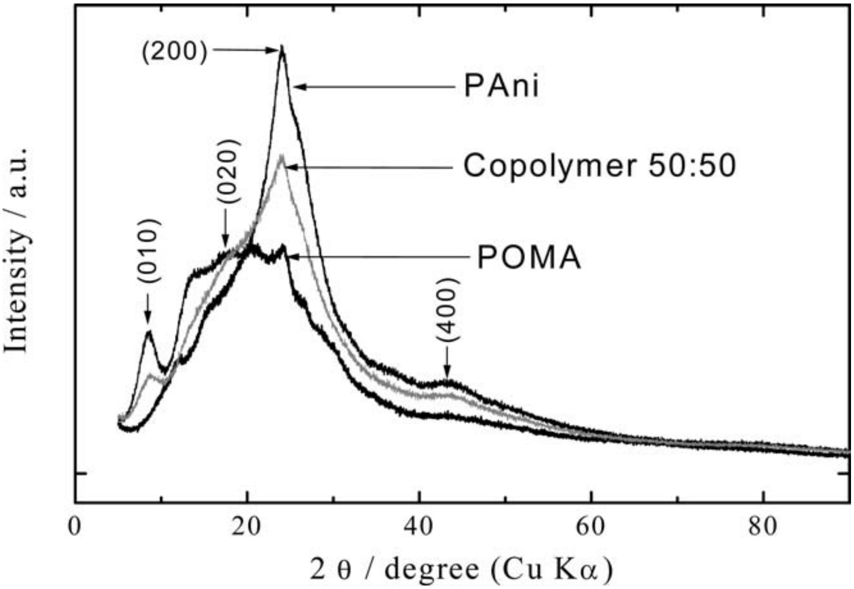


FIGURE 2 X-ray diffraction patterns of PAni, POMA and the copolymer 50:50.

as corrosion protection in their EB and ES forms. The potentio-dynamic polarization curves shows that EB-forms coating imparts the best protection in 0.01 M NaCl solution, that is the open circuit potentials shift to more noble values compared to the bare alloy and the corrosion current densities are one order of magnitude lower than that of uncovered alloy. Further the good barrier property of EB before polarization curve measurement remains almost the same after measurement of the curve. Its excellent resistance to the Sellotape-Test confirmed after corrosion test is due the optimum polymer load in the ink and the preparation procedure. By contrast, the-salt forms did not bring about advantages and were less resistant to Sellotape-Test than the EB-forms.

It is believed that ($^{-}OCH_3$), an electron-withdrawing radical, adsorbs strong to a metallic substrate (high coverage). This fact can support the better corrosion inhibition of copolymers than PAni.

c) Corrosion Mechanism

The actual accepted mechanism for the protection of aluminum is

$$2Al + 3H_2O = Al_2O_3 + 6H^+ + 6e$$
$$3ES + 6H^+ + 6e = 3LS$$
$$3LS = 3LB + 6H^+$$

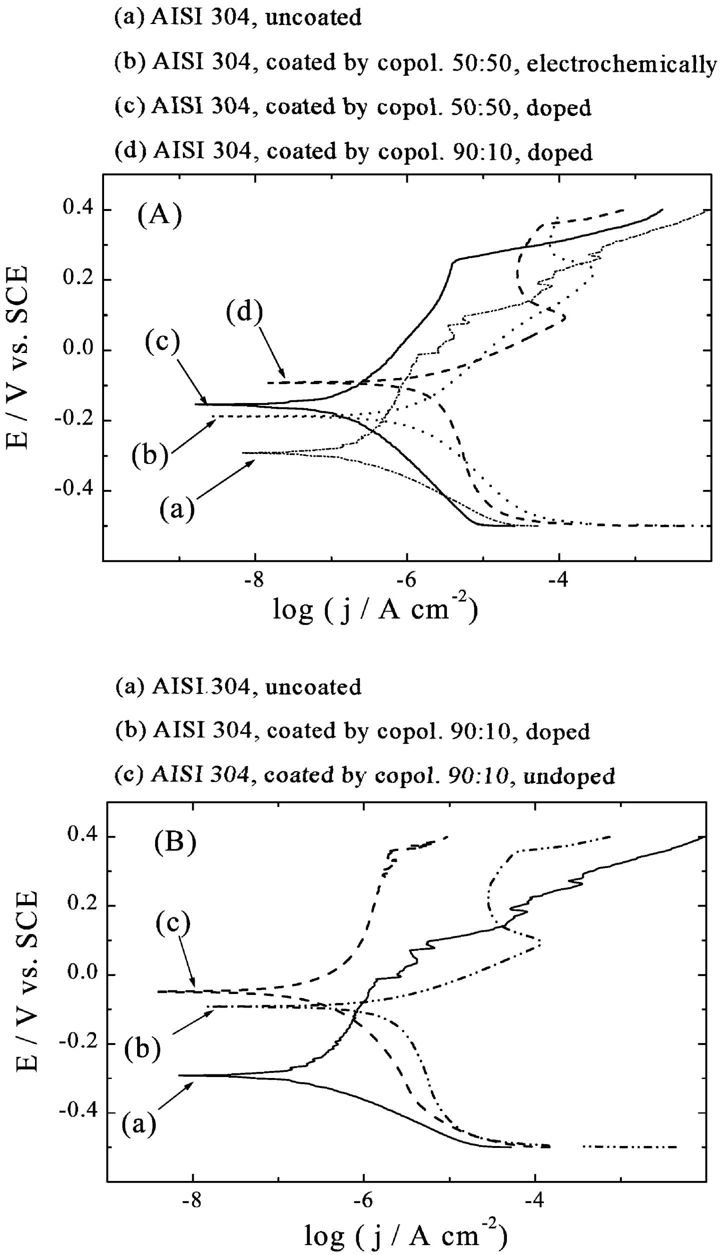


FIGURE 3 Polarization curves of: (A) the copolymer coatings on AISI 304 in 3% NaCl (0.5 M) in doped states and (B) the copolymer 90:10 in doped and undoped forms. Uncoated substrate constitutes the reference.

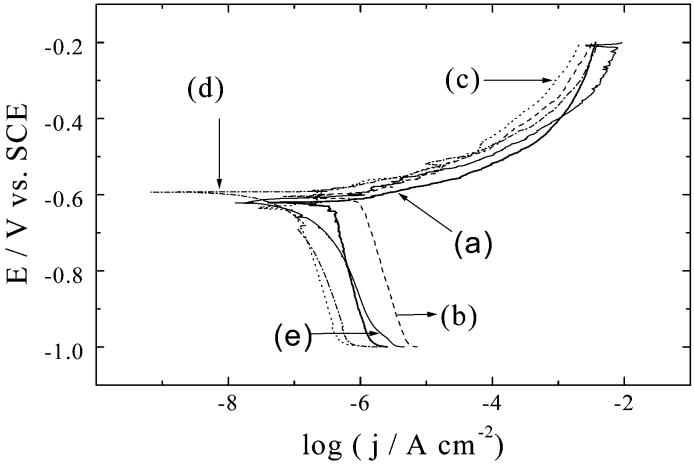


FIGURE 4 Polarization curves of (a) PAni, (b) POMA and, (c) 40:60 and (d) 60:40 copolymers in 0.01 M NaCl (pH = 6.02). The (e) bare alloy is taken for comparison.

where ES is the emeraldine salt, LS the leucoemeraldine salt and LB the leucoemeraldine base.

Aluminum oxide is formed by a partial reduction of the high conductive emeraldine salt to its less conductive form leucoemeraldine salt. This is manifested as change of color from green emeraldine salt to pale leucoemeraldine salt. LS reduces to LB by losing protons.

Similar reactions can be written for corrosion of steels, with the formation of Fe_2O_3, as reported in this journal [15].

d) Scheme of Protection

As reported elsewhere [16], an optimum coating formulation comprises a electrochemical polymer formed from 0.1 M aniline in 0.52 M oxalic acid (PAni in this example) followed by a top coat which can consist of epoxy

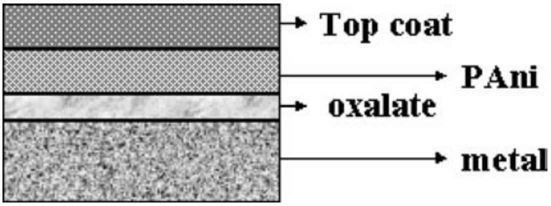


FIGURE 5 PAni-oxalate coating on aluminum with a top coat.

resin. In this type of coating, an excellent adhesion is due to the thin layer of oxalate with dispersed PAni.

CONCLUSIONS

Polymer coatings on AISI 304 and aluminum alloy 6061-T6 offer corrosion protection owing to the ennoblement of the corrosion potential compared to the uncoated substrate. Copolymerization offers a further but little ennoblement of the corrosion potential and its solubility in common solvents remains a challenge. In the case of steels the protection is anodic, while for aluminum and its alloys not. Following conclusions are drawn from the results:

1. Copolymer-coatings on AISI 304 perform better than PAni by making the material more noble compared to the uncoated material and even pure PAni. Their base forms present a further advantage in decreasing their corrosion current densities.
2. POMA is amorphous in structure and PAni is crystalline. Otherwise, the copolymer 50:50 only said has a structure less crystalline than PAni.
3. Copolymers poly (ani-co-o-methoxianiline) produce adherent films by painting EB-solutions in NMP. The electrochemical counterpart films are more adherent than the paintings due to avoiding coalescence.
4. On aluminum alloys, a marked ennoblement of the corrosion potential is not observed as on steels, although the copolymer 60:40 presents the most ennobled potential.

REFERENCES

[1] DeBerry, D. W. (1985). *J. Electrochem. Soc.*, *132*, 1022.
[2] Thompson, K. G., Bryan, C. J., Benicewicz, B. C., & Wrobleski, D. A. (1995). Los Alamos National Laboratory Report LA-UR-92-360: *Polym. Preprints*, *35*, 265.
[3] Wessling, B. (1994). *Adv. Materials*, *6*, 226.
[4] Lu, W. K., Elsenbaumer, R. L., & Wessling, B. (1995). *Synth. Met.*, *71*, 2163.
[5] McAndrew, T. P., Miller, S. A., Gilicinski, A. G., & Robertson, L. M. (1996). *Proc. Am. Chem. Soc., Div. Polym. Mater. Sci. Eng.*, *74*, 204.
[6] Camalet, J. L., Lacroix, J. C., Aeiyach, S., Kane-Ching, K., & Lacaze, P. C. (1988). *Synth. Met.*, *93*, 133.
[7] Senthurchelvan, R., Wang, Y., Basak, S., & Rajeshwar, K. (1996). *J. Electrochem. Soc.*, *143*, 44.
[8] Racicot, R. J., Clark, R. L., Liu, H.-B., Yang, S. C., Alias, M. N., & Brown, R. (1996). *Mat. Res. Soc. Symp.*, *413*, 529.
[9] Epstein, A. J., Smallfield, J. A. O., Guam, H., & Fahlman, M. (2000). *Synth. Met.*, *102*, 1374.
[10] Bierwagen, G. (2001). *J. Coat. Technol.*, *73*, 45.
[11] Ye, S., Do, N. T., Dao, L. H., & Vijh, A. K. (1997). *Synth. Met.*, *88*, 65.

[12] Prévost, V., Petit, A., & Pla, F. (1999). *Synth. Met.*, *104*, 79.
[13] Ram, M. K., Sarkar, N., Ding, H., & Nicolini, C. (2001). *Synth. Met.*, *123*, 197.
[14] Santos, J. R., Jr., Mattoso, L. H. C., & Motheo, A. J. (1998). *Electrochim. Acta*, *43*, 309.
[15] Moraes, S. R., Huerta-Vilca, D., & Motheo, A. J. (2002). *Mol. Cryst. Liq. Cryst.*, *374*, 391.
[16] Domingo Huerta-Vilca, Sandra R. Moraes, & Artur J. Motheo, (2003). *J. Braz. Chem. Soc.*, *14*, 52.