Rev. Téc. Ing. Univ. Zulia, Vol 16, No. 2, 101-109, 1993

Study of the influence of the weight average molecular weight of Poly(N-vinylimidazole) in corrosion protection of copper in acetate buffered media by cyclic voltammetry

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Abstract

N-heterocyclic compounds, as such or as side chains of water-soluble polymers, are well-known for their ability to inhibit corrosion on copper. Here it is reported on the inhibitory capacity of poly(N-vinylimidazole), and on how this capacity in affected by the molecular weight of the carrier polymer. Three different polymer samples, DP_w 1,170, 6,800, and 17,400 respetively, were prepared by free-radical, vinyl polymerization, and characterized by viscosity measurements. The studies, carried out by cyclic voltammetry, show a linear dependence of the inhibitory capacity on molecular weight, whereby, an interpretation is discussed based on the hydrodynamic volume of the polymer coils in solution, which depend on the 1.5 power of the molecular weight. Thus, during the evaporation of the polymer solutions, to form the protective films, those with larger molecular weights will reach the critical concentration, on which the molecular coils begin to impinge on each other, at an earlier stage of the process. This, in turn, should lead to a more efficient interpenetration of the coils and, eventually, to films with better physical stability and improved inhibitory capacity.

Key words: Inhibitor, Poly(N-vinylnidazole), Corrosion, Copper

Estudio de la influencia del peso molecular promedio del Poly(N-vinylimidazole) en la protección del cobre en solución amortiguadora de acetato por medio de la voltametría ciclíca.

Resumen

Los compuestos N-heterocíclicos, por si mismo o como cadenas laterales de polimeros solubles en agua, son bien conocidos por su capacidad de inhibir la corrosión del cobre. En este trabajo se da a conocer la capacidad inhibidora del Poly(N-vinilimidazole) y como esta capacidad es afectada por el peso molecular del polimero transportador.

Se prepararon tres muestras de polímeros diferentes cuyos pesos moleculares eran de 1170, 6800 y 17400, utilizando una polimerización vinílica de radicales libres, y se caracterizaron por medidas de viscosidad. Los estudios realizados por voltametría cíclica, demostraron que hay una lineal de la capacidad inhibidora con el peso molecular; por lo cual, se da una interpretación basada en el volumen hidrodinámico del polímero en solución, que depende del peso molecular a la potencia 1.5. Así, durante la evaporación de las soluciones poliméricas, para formar películas protectoras, aquellas con mayores pesos moleculares alcanzaron una concentración crítica, en la cual las cadenas moleculares empiezan a chocar entre si desde el inicio del proceso. Esto, en cambio, conduciría a una interpretación más efectiva de las cadenas y, eventualmente, a películas con mejor estabilidad física y capacidad inhibidora mejorada.

Palabras Claves: Inhibidor, Poly(N-vinilinidazole), Corrosión, Cobre.

Introduction

N-heterocyclic compounds have been used as corrosion inhibitors on copper for several decades. Azole compounds such as benzotriazole[1-6], benzimidazole, indazole and imidazoles[7-12] were the most widely used in corrosion protection of copper and copper based alloys and has been the subject of many investigations.

Inhibitors mentioned above are small molecules in nature. Recently there has been great interest in using water soluble polymers with heterocyclic side groups as corrosion inhibitors for copper in high-temperature atmospheric enviroments.

Eng and Ishida[13,14] employing Fourier transformed infrared reflection absorption spectroscopy (FTIRRAS) reported that polyvinylimidazoles (PVI_s) are effective new polymeric antioxidant agents for copper.

In the present study, cyclic voltammetry techniques were used to determine the influence of the weight average molecular weight of Poly(N-vinylimidazole), PVI(1), on the copper inhibition in acetate buffered media, and the effects of pretreatment of copper surfaces with ethanolic solutions in p.p.m of the $PVI(1)_s$ at room temperature and with thermal treatment in the range from 60° to 250° C during 15 minutes.

Although the behaviour of imidazole on copper has been reported, PVI(1) have the imidazole ring as their pendant group which would lead to complexes formation with copper. The ability of these polymers to bind metals presumably should be affected by the conformational behaviour of the $PVI(1)_s$[15].

Furthermore the use of bidentate ligands has been known to produce much higher equilibrium constants in favor of the complexed metal. By tying many such ligands together in the form of a polymer, the complexed copper will be prevented from leaving the surface.

Lastly, it is known that polymers can easely form thin films of high ductility enhancing the adhesion of the films to the substrate.

Experimental Methods and Materials

a- Synthesis of Poly(N-Vinylimidazoles)

Three PVI(1) were synthesized to obtain different molecular weights (weight average) by polymerization of the purified distilled monomer N-vinylimidazole (N-VI), 0.1067 mol dissolved in 70 ml of benzene with different amounts of purified Azobis (isobutiro-nitrile), (AIBN), obtained by recristallization in an ice bath of crude AIBN dissolved in warm methanol, (2.6×10^{-4} mol $\leq$ AIBN $\leq 2.2 \times 10^{-3}$ mol).

The polymerization times of N-VI and AIBN in benzene heated at reflux with stirring under nitrogen, were of 24,48 and 72 hours. The polymers precipitated as white powders were collected by filtration, washed three times with benzene at room temperature and dried in a vacuum oven (20 mm Hg) at 35° C.

b- Intrinsic viscosity measurements

The characterization of PVI(1) in regard to molecular weight was achieved by viscosimetry[16]. NaCl 0.5 M solutions performed as solvent media, and the measurements were carried out with the help of an Ostwald capillary viscosimeter 0.04 cm in diameter, at a temperature of 25° C. In order to calculate the "intrinsic viscosity" from the experimentally obtained "viscosity numbers", they were extrapolated to zero concentration by means of the Schulz-Blaschke method[17], whereby the necessary value of $k\eta$ = 0.40 was established by measuring one of the PVI(1) samples at four different concentrations.

Viscosity-average molecular weights (almost identiacal numerically to the corresponding weight-average figures), were then derived from the intrinsic viscosities by means of the Mark-Houwink-Sakurada equation $[\eta] : KM_{\eta}^{-a}$, whereby K: 0.12 and a: 0.5 were obtained from the literature[18].

c- Electrochemical measurements

Experiments were done using a pyrex glass conventional three compartments double wall electrolysis cell. The working electrodes were cut from OFHC 99.99% pure polycrystalline Cu rod (OD :0.4 cm), axially embedded in a p.t.f.e holder to make a still Cu disc of an exposed surface area of 0.216 cm^2.

Previous to each run the surface of the electrodes were mechanically polished beggining with 600 mesh emery paper to finish with a mirror surface using 0.3 μm alumina powder. No attempt was made to prevent the freshly polished electrode from contacting air, previously casting them with ethanolic solutions of the three PVI(1) (I, II and III) containing 20 ppm of each polymeric inhibitor, air dried and heat treated at 130° C for 15 minutes. A saturated calomel electrode (SCE) was used as reference, the counter electrode was a Pt sheet. The acetate buffer solution used as electrolyte (pH : 6.0), was prepared with sodium acetate 2.8 M, acetic acid: 0.05 M, at 30° C oxygen freed by bubbling with purified nitrogen. Fresh electrolyte was used in each electrochemical rum.

Cyclic voltammetry was performed using a LYP M-6 voltammeter and voltammograms were recorded using a Philips PM 1834 x-y recorder. The scan rates (v) were $0.005 \leq v(V\ s^{-1}) \leq 0.50$, but the voltammetric sweep rate of 0.20 V s^{-1} was employed and used as a basis for comparison to determine the inhibition efficiency.

The voltammetric sweep range spanned from -0.90 to + 0.90 V (SCE).

This potential range includes the formation of soluble and insoluble products characterized by different peaks apparently associated with multiple electrode processes as suggested by the shape and structure of the peaks.

Results and Discussion

Cyclic voltammetry measurements on polycrystalline copper

Figure 1 shows the voltammogram obtained from uncoated polished copper in the acetate buffer solution with the typical oxidation processes leading to the formation of the soluble species $Cu(OH)_2$-(19) (peak A) with a potential negative to peak B associated with the formation of Cu_20[20,21]. Peak C is generally associated with the formation of Cu(II) species with the production of CuO and/or $Cu(OH)_2$(22).

The cathodic peaks D and E, obtained in the sweep reversal experiments support the conclusions reported in the literature[19,23], with the reduction of Cu(II) to Cu(I) (Cu_2O), and Cu(I) to Cu respectively.

It is interesting to noticed the different behaviour between the first cycle (a) and the succesive multiple sweeps indicated in the figure. The appearance of an anodic peak at the potential value of peak A, during the cathodic sweeping can be assigned to the formation of Cu(I) by the chemical deprorportionation reaction between Cu^{2+} species and Cu from the partially uncovered electrode. Anodic and cathodic peak currents increase rapidly in magnitude during cycling due to an increase in surface area.

Cyclic voltammetry measurements on coated polycrystalline copper with PVI(1)s

The cyclic voltammogram shown in Figure 2 is given as an example of the numerous experiments carried out with the coated copper electrodes obtained by casting with the ethanolic solutions of 20 ppm of the three polymers (PVI(1), I, II and III, Table 1) and with heat treatment at 130° C during 15 minutes.

The E/I profiles obtained with the organic polymer are quite different in comparison with the uncoated electrode. Even in the classical peaks mentioned above (Fig. 1), the peak currents decrease in magnitude with continuos cycling up to 20 cycles, indicating the inhibition phenomena.

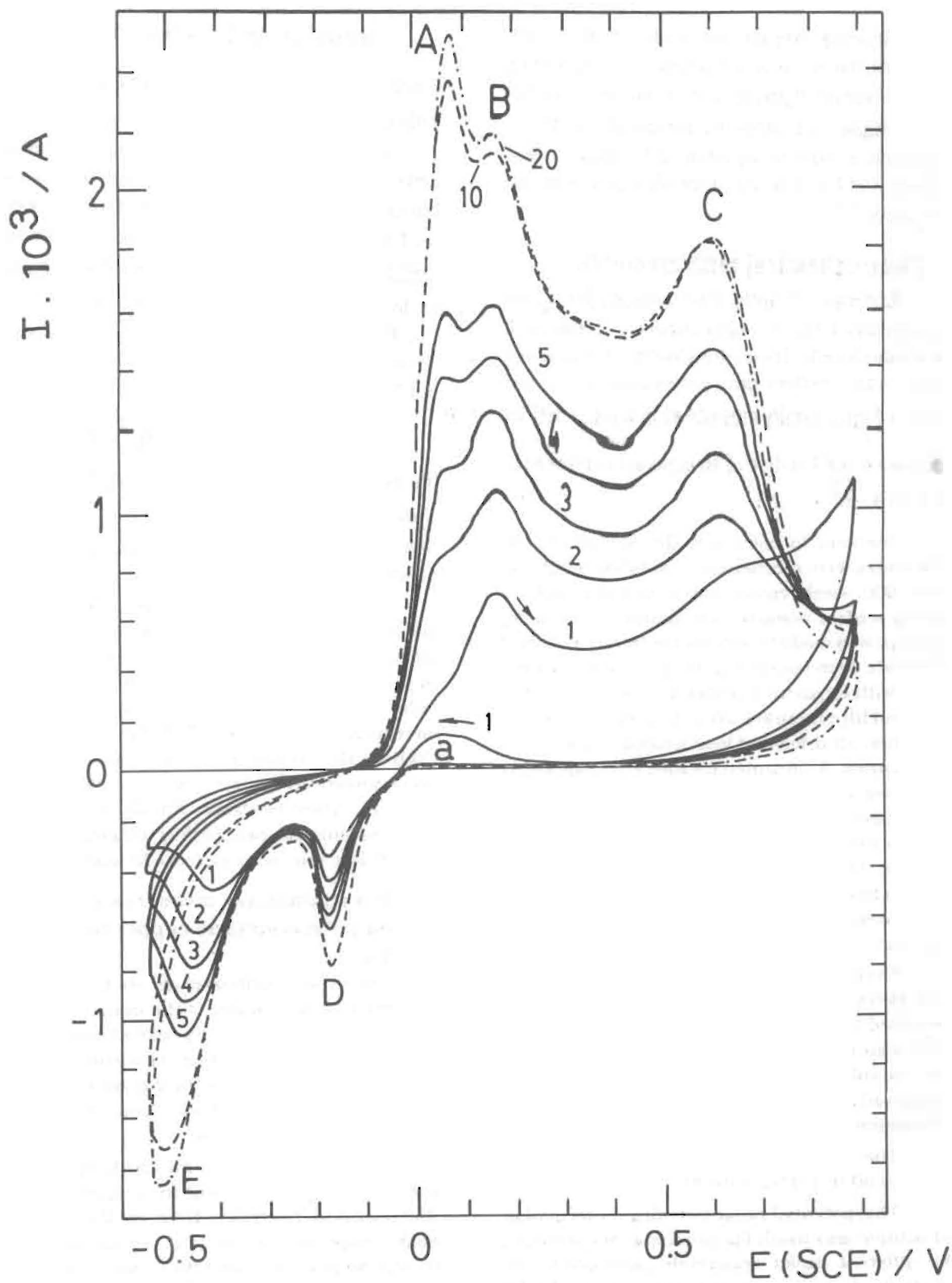

Figure 1: Triangular sweep voltammogram for a polycrystalline copper electrode in acetate buffer solution pH: 6.00, 30 °C, sweep rate (v) of 0.20 Vs^{-1}. Apparent surface area 0.216 cm^2.

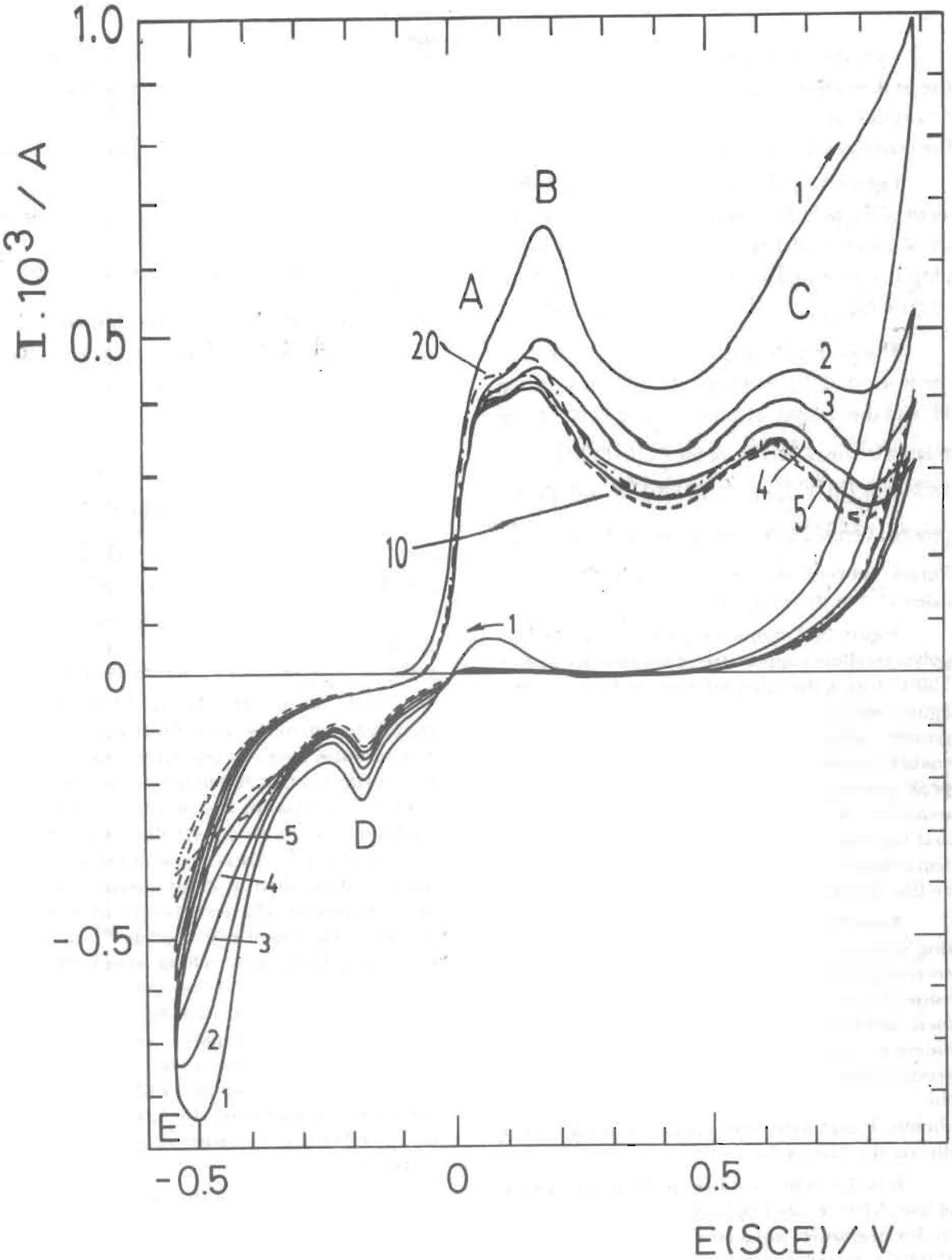

Figure 2: Triangular sweep voltammogram for a polycrystalline copper electrode coated with PVI-III, 20 ppm, heat treated at 130 °C during 15 minutes in acetate buffer solution pH: 6.00, 30 °C, sweep rate (v) of 0.20 Vs^{-1}. Apparent surface area 0.216 cm^2.

By further increasing the number of cycles the peak currents started growing indicating the desorption of the organic coating material with the consequent loss of copper protection.

Figure 3 (a) shows the voltammetric behaviour of the polymers coated copper electrodes in the stagnant buffer electrolyte cathodically sweeping the potential from the rest potential (c.a. -0.10 V (SCE) to -0.95 V (SCE) at v: 0.005 Vs^{-1}.

The peak potentials are practically the same (c.a. -0.52 V/(SCE)) for the $PVI(1)_s$ I, II and III, and the charges involved near to $2x10^{-3}$ C are related to the reduction of the $Cu(I)/PVI(1)_s$ complexes to $Cu/PVI(1)_s$, controlled by a diffusion process verified from the linear relationship obtained between the peak currents and sweep rates $v^{1/2}$ in the range of 0.005 to 0.50 Vs^{-1}.

Figure 3(b) shows the peaks obtained with polycrystalline copper electrodes heat treated at 130°C during the different times indicated in the figure, which gradually induced the Cu_2O film growth, with the object to compare with the coated copper electrodes mentioned above. The peak potentials corresponding to the cathodic reduction of Cu_2O to Cu are c.a. -0.34 V/(SCE), and the charges involved increased with the extent of heat treatment following a typical parabolic film growth law[23].

In both experiments with the polymer coating and the naked copper electrodes no peaks corresponding to the cathodic reduction are obtained from the second cycle on. This is in agreement with the fact that Cu(I) species forming bidentate complexes with the vinylimidazole groups bound to the main polymer chain, and the Cu(I) of the Cu_2O produced by previous chemical oxidation are wholly reduced to Cu during the first cycle.

It is also of interest to remark the behaviour of the $PVI(1)_s$ coated polycrystalline copper electrodes previously subjected to a heat treatment at 250° C for 15 minutes.

The voltammograms showed the dissappearance of the peak corresponding to the reduction of the Cu(I) $PVI(1)_s$ complexes (Fig. 3a) indicative of the pyrolitic destruction of the polymeric coatings. The free Cu(I) layer in the form of Cu_2O, in turn, originates the typical reduction peak at -0.34 V (SCE), (Fig. 3b), in agreement with observations derived from FTIRRAS[13,14].

Inhibiting efficiency and molecular weight

The inhibiting efficiency (ε %) is defined as $\varepsilon\%: \left(1-\frac{I_i}{I_0}\right)$ x 100, with I_i and I_0 the measured currents after 10 cycles with and without inhibitor respectively of peaks 2 (Fig. 2 and 1), associated with the formation of Cu_2O, chosen as reference.

The results show that ε% increases linearly with molecular weight ($\overline{MW}$) in the range of degree of polimerization ($\overline{DPw}$), as determined by intrinsic viscosity measurements (Table 1).

The linear dependence between ε% and $\overline{MW}$ must derive from properties of the system directly ascribable to their macromolecular nature.

Since on the other hand, the specific chemical interactions between Cu(I) and vinylimidazole residues have not reason to depend in $\overline{MW}$, it is suggested that the inhibitory action derives from an increase in the physical stability and continuity of the polymeric films with growing molecular weight. Thus, the well-known average macroconformation of linear polymers in solution, mathematically described by means of the so-called "statistical coil" models[24], determine that the hydrodynamic volume of individual molecules in solution increases with the 3/2 power of the $\overline{MW}$, instead of depending linearly on it, as it is the case for collapsed solid molecules. In solutions with the same mass concentration of $PVI(1)_s$, then, those samples with larger $\overline{MW}$ will reach upon evaporation the "critical concentration" condition at an earlier stage of the process (Table 1).

As evaporation of the solvent proceeds, then the larger molecules will begin to interprenetate which each other and reach a sizable degree of intermolecular, physical entanglement before the smaller ones do, which in turn should account for the suggested improvemment in stability of the coating. In fact, through "irreversible entanglement" the molecules lose their indivi-

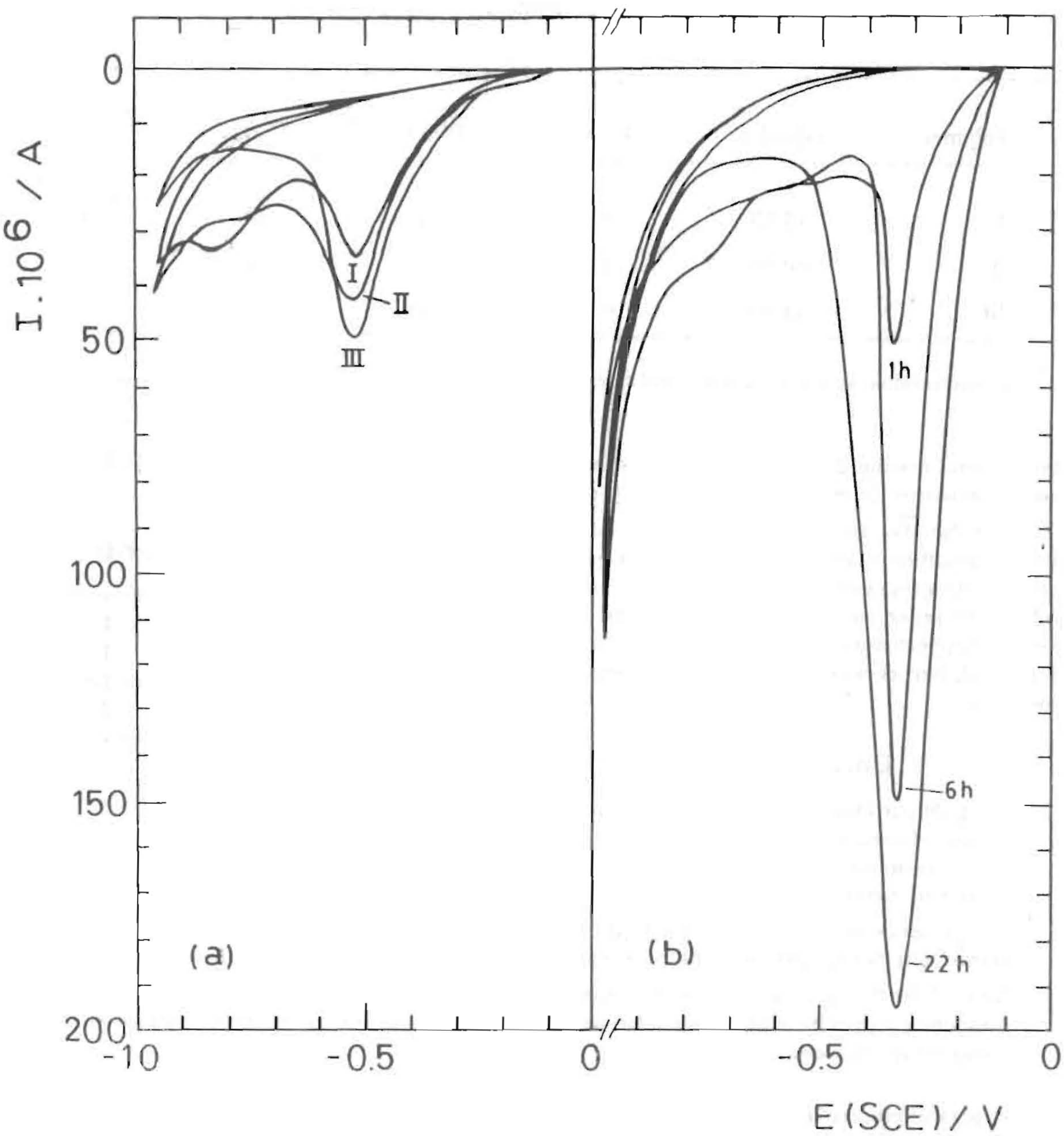

Figure 3: Potentiodynamic charging curves, sweep reversal from the rest potentials in acetate buffer solutions pH: 6.00, 30 °C, sweep rate (v) of 0.005 Vs^{-1}.

(a) Polycrystalline copper electrodes coated with PVI- I- II and III, 20 ppm, heat treated at 130 °C for 15 minutes. Apparent surface area 0.216 cm^2.

(b) Polycrystalline copper electrodes, heat treated at 130 °C at different times (hours) indicated in the figure.

Table 1

Polymer	$[\eta]/ml\ g^{-1}$	$\overline{MW} \times 10^{-5}$	$\overline{DP}_w \times 10^{-3}$	C^*/gl^{-1}	$\varepsilon\% \pm 4\%$
I	40.25	1.10	1.17	25	16
II	96.53	6.40	6.80	10	42
III	153.60	16.4	17.40	6	95

C^*: the concentration at which the individual macromolecular coils begin to impinge which each other.

duality and become for all practical purposes, a continuous two-dimensional molecular layer.

As the $\overline{MW}$ decreases, on the other hand, the C^* condition is reached at a more advanced stage of the evaporation process, with the concomitant increase in solution viscosity and the reduced opportunities for the intermolecular interprenetation of segments that leads to entanglement.

Conclusions

- The polymer film covering the surface of the copper electrode, obtained by casting and heat treatment, complactly acts as a true barrier to further copper oxidation.
- The presence of Cu_2O enables the formation of the Cu(I) $PVI(1)_8$ surface inhibitor complex.
- None of the $PVI(1)_8$ (I, II and III) is suitable for protecting copper by simple immersion in the complexing solutions.
- Cyclic voltammetry is a useful technique to study inhibition efficienty and degradation of the polymeric coatings, as it allows to identify the complexed and non complexed nature of Cu(I) by means of the differnt reduction potentials respectively.
- The inhibition effect of the polymeric coatings derives from two basic mechanisms: i) The complexing of Cu(I) by the pendant imidazole side chains, independent of molecular weight, and ii) The entanglement of the polymer coils whose hydrodynamic volume in solution depends on the 1.5 power of the molecular weight.

Acknowledgements

This research project was finantially supported by the Consejo Nacional de Investigaciones Científicas y Técnicas (CONICET) and the Comisión de Investigaciones Científicas de la Provincia de Buenos Aires (CIC). R.C.V. Piatti is a member of the Professional Career of CIC.

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