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Effect of hydrochloric acid on the transport properties of tin through ion-exchange membranes

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ABSTRACT

This work presents a study of the transport properties of two ion-exchange membranes present in an electrochemical reactor used to process the wasted and rinse baths of the electroless plating of polymers industry. The influence of the hydrochloric acid on the transport properties of tin through both cation- and anion-exchange membranes has been evaluated by chronopotentiometry. The shape of the chrono-potentiograms depends on the specie under consideration, Sn(II) or Sn(IV), the hydrochloric acid concentration and the type of membrane. In the case of the study of Sn(II) transfer through the cation-exchange membrane (CEM), the contribution of the water splitting is evident for every HCl concentration by the increase of the membrane potential drop (E_m) after a short-time plateau observed in the chronopotentiograms, and by the appearance of a $Sn(OH)_2$ precipitate located at the anodic solution-membrane interface. The transport of Sn(IV) through the CEM is a complex phenomenon due to their high charge density leading to an important hydration shell, to their low mobility and, to their trend to form hydroxyl complexes and insoluble salts. Low HCl concentrations and high applied currents leads to the formation of a Sn(IV) specie, probably the $Sn(OH)_6^{2-}$ monomer, which can polymerise and remain adhered to the membrane surface. This specie is re-dissolved when the HCl concentration is increased. In the case of Sn(II) transfer through the anion-exchange membrane (AEM), if the applied current is high and the HCl concentration is low, the OH- produced due to water splitting are forced to cross the membrane when the chloride concentration in solution is depleted. For higher HCl concentration, the development of the gravitational convention phenomenon is coupled with the water splitting at those high applied currents. The presence of Sn(IV) at low HCl concentration in the over-limiting region produces a diffusion-relaxation region characteristic of the bipolar membranes. The formation of a Sn(IV) gelatinous specie adhered to the anodic side of the AEM could explain the formation of the bipolar structure in the membrane. At lower pH values the formation of this Sn(IV) gelatinous specie is avoided, and the OH- ions from the water splitting are responsible for the peak of E_m observed in the chronopotentiograms.

Keywords: Anion-exchange membrane; Cation-exchange membrane; Chronopotentiometry; Hydrochloric acid; Sn(II); Sn(IV); Water splitting

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1. Introduction

In the last years, ion-exchange membrane processes have been suggested as a promising possibility for the removal and the recovery of heavy metals and other inorganic toxic substances generated in electroplating processes [1–3]. In this context, the tin present in the activating wasted solutions and the rinse water baths of the plating of polymers industry can be effectively recovered using an electrochemical reactor with two compartments separated by an ion-exchange membrane. The presence of separators in electrochemical reactors is essential when reagents or products of one electrode process are susceptible to reaction at the counter electrode [4]. In our particular case, the use of a separator is justified in order to prevent the oxidation of Sn(II) at the anode which would lead to the loss of current efficiency in the overall process. However, the presence of a separator in an electrochemical reactor introduces an ohmic drop which contributes to the increase of the overall cell voltage. This ohmic drop has to be minimized since energy inputs and electricity costs are directly affected by the cell voltage [5].

In electromembrane processes it is desirable to work at high current densities in order to achieve high efficiency with the lowest possible effective membrane area. In practice, however, operating currents are restricted by the occurrence of concentration polarization. This phenomenon, which is defined by the current-induced concentration gradient occurring near the membrane/solution interface [6,7], may lead to operational problems such as the precipitation of inorganic salts, the destruction of the membrane and an increase in the energy consumption, causing a decrease in the effectiveness of the process [8].

In the case of the activating solutions of the electroless plating of polymers, they are mainly composed of $SnCl_2$ and $PdCl_2$ in HCl as diluting agent, where tin is the major species. As a consequence of palladium reduction, and because of direct oxidation by air, Sn(II) is oxidized to Sn(IV). In the case of the rinse water baths, although the HCl concentration is lower, the big volumes generated represent an important problem of treatment and disposal. Hence, the present paper evaluates the influence of the chloride ions on the transport properties of tin through ion-exchange membranes for a concentration range of chlorides, similar to that occurring in the concentrated wasted baths and in the diluted rinse solutions.

On the other hand, besides the Sn(IV)–Cl complex species formed in solution, both Sn(II) and Sn(IV) present a high tendency to form hydroxylated complex species at moderate pH values [9,10]. Since those complex species may be positively or negatively charged, the present work evaluates the transport properties of tin through both cation- and anion-exchange membranes as a function of chloride concentration by means of chronopotentiometry. This technique consists of applying a current pulse and measuring the response of the potential drop across the membrane as a function of time.

2. Theory

Chronopotentiometry is an electrochemical characterization method that measures the electric potential response of a system to an imposed current. Besides, it allows obtaining information regarding with the membrane heterogeneity, transport number of the ions through the membranes and limiting current density [11–23].

The chronopotentiograms represent the potential difference between two reversible measured electrodes installed in solutions at both sides of the membrane as a function of time. The classical chronopotentiogram is represented in Fig. 1 and is composed of four sections: the first one, region 1, is practically vertical, its height is equal to the ohmic potential drop due to the current imposed and the slope depends on the capacity of the electric double layer at the membrane/solution interface. The second section, region 2, corresponds to a slow growth of the potential up to the inflection point. It is due to the decrease in the concentration in the depleting solution near the membrane governed mainly by electro-diffusion processes. After passing the inflection point, region 3, other mechanisms of the matter transfer to the membrane surface, mainly convection, become important. Note that the inflection point exists only when the applied current is higher than the limiting one. Finally, the system reaches a steady state where the potential varies no more with time, section 4. The potential breakdown obtained immediately after switching-off the current (region 5) corresponds to the ohmic potential drop over the polarised membrane system. The last region, referred to as region 6, describes the diffusion relaxation of the system [12].

An important characteristic of the non-stationary ion transfer process is the transition time, τ. This time corresponds to the moment where the interfacial concentration becomes zero, the potential tending to infinity. As in real processes the potential does not tend to infinity, there is a certain problem how to find the transition time from the measured chronopotentiograms. Some authors [23,24]

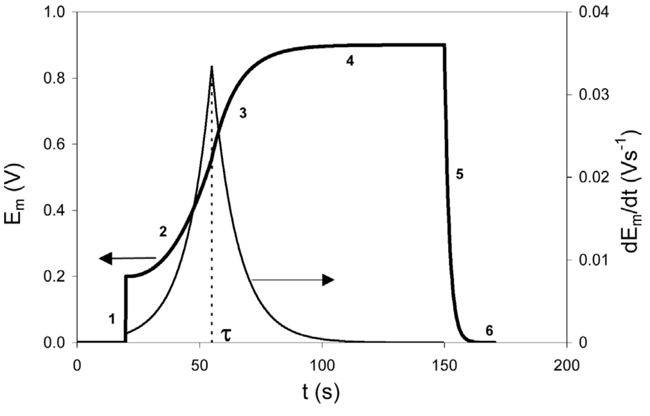

Fig. 1. Characteristic shape of a chronopotentiometric curve obtained for a current intensity above the limiting current intensity.

interpret the inflection point time as the transition time which is graphically determined from the derivative of the membrane drop as a function of time as shown in Fig. 1 [4]. On the other hand, this parameter may be calculated by means of the Sand's equation:

$$\tau = \frac{\pi \cdot D}{4}\left(\frac{z \cdot \mathrm{F}}{\bar{t}_i - t_i}\right)^2 \left(\frac{C_0}{i}\right)^2 \quad (1)$$

where C_0 is the concentration of the counter-ion in the bulk, i is the current density, D is the electrolyte diffusion coefficient, z the charge of the counter-ion, $\bar{t}_i$ and t_i are the transport numbers of the counter-ion in the membrane and in the solution, respectively, and F the Faraday's constant. Eq. (1) shows that the transition time is proportional to the inverse of the current density squared and that the transition time increases when the membrane transport number decrease, i.e. when the membrane is less permselective.

A typical example of a current–voltage curve is represented in [25], in which the concepts of limiting current and overlimiting region are defined. A theoretical expression for the limiting current density is also presented in this paper.

3. Experimental

The schematic diagram of the two-compartment electrochemical cell was presented in [25]. The cell was composed of two 250 ml symmetrical half-cells between which the ion-exchange membrane was clamped. The cation- and anion- exchange membranes are referenced as Ionics CATION 67-HMR-412 and Ionics ANION-204-SXZL-386, respectively. The main properties of these membranes are also described in [25].

Two Ag/AgCl flat electrodes were used to impose the current and two Ag/AgCl reference electrodes immersed in Luggin capillaries were used to measure the potential drop through the membrane, E_m. The constant current was supplied by Tacussel Electronique PJT-120-1 potentiostat/galvanostat. The membrane potential and the imposed current were registered using a PC data acquisition system. All experiments were conducted at room temperature and without stirring and were carried out after a membrane equilibration period of at least 24 h using a solution with the same characteristics as that used in the experiments.

Since Sn(II) is progressively oxidized to Sn(IV) in the activating solutions, synthetic solutions of Sn(IV) and Sn(II) from analytical reagent grade $SnCl_4 \cdot 4H_2O$ and $SnCl_2 \cdot 2H_2O$ were prepared. The selected tin concentrations were similar to that occurring in the real solutions and were in the range of 10^{-2} M. The HCl concentration range under study varied from 10^{-3} to 10^{-1} M in order to reproduce its real concentration in the wasted and rinse baths. The applied current pulses depended on the electrolyte concentration and on the ion-exchange membrane under study.

4. Results

4.1. Effect of hydrochloric acid on the transport of tin through the cation-exchange membrane (CEM)

The chronopotentiometric curves obtained in the cation-exchange membrane for 0.01 M $SnCl_2$ when the HCl concentration is 10^{-2} M and 10^{-1} M are illustrated in Figs. 2 and 3, respectively. When the current intensity is small there is no inflection point in the chronopotentiometric curve: a steady state is achieved at an interfacial concentration, which is of the same order of magnitude as the bulk concentration. The inflection point appears when the interfacial concentration becomes relatively low to give a rapid rise to the membrane potential drop. In this case the electro-diffusion through a stagnant diffusion layer is not sufficient to compensate the deficit in salt produced by the difference in electro-migration transport numbers in the membrane and the solution. The CEM in contact with the 0.01M $SnCl_2$ and 10^{-2}M electrolyte (Fig. 2) presents a limiting current at about 45 mA, hence the chronopotentiograms obtained at lower current intensities (40 mA) does not shown any inflection point, whereas for applied currents above 45 mA, such as 50 and 80 mA, characteristic transition times are observed.

On the other hand, Fig. 2 also shows a maximum of membrane potential (E_m) when the applied current is 50 mA. After an abrupt increase of E_m, corresponding to the ohmic drop between the two reference electrodes, the membrane potential decreases due to the presence of protons in the anodic compartment. These protons are produced as a consequence of the water dissociation process, which takes place in the overlimiting region, and are transferred through the CEM preferentially to Sn(II) due to their higher mobility. They progressively replace tin ions balancing the cation-exchange membrane, and

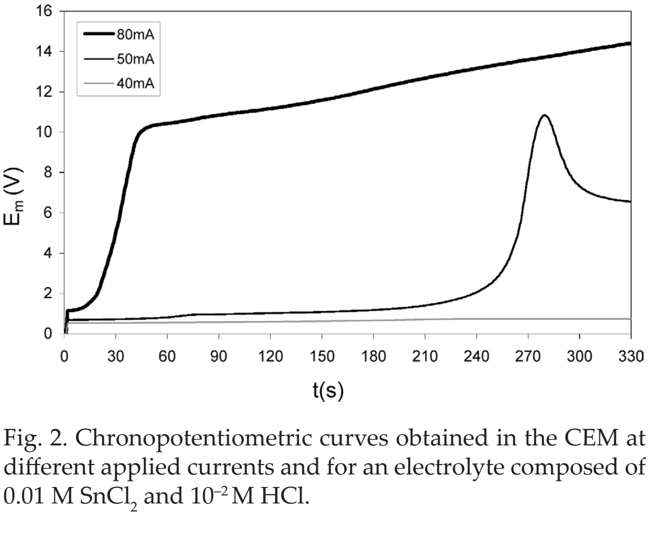

Fig. 2. Chronopotentiometric curves obtained in the CEM at different applied currents and for an electrolyte composed of 0.01 M $SnCl_2$ and 10^{-2} M HCl.

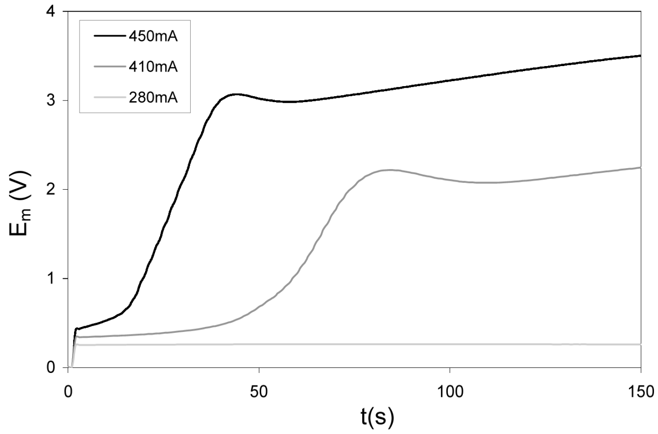

Fig. 3. Chronopotentiometric curves obtained in the CEM at different applied currents and for an electrolyte composed of 0.01 M $SnCl_2$ and 10^{-1} M HCl.

consequently, the ohmic resistance of the CEM decreases until a dynamic equilibrium of the H^+/Sn(II) partition within the membrane is reached. At this time, the membrane potential does not vary any more. For higher current densities, about 80 mA, no stationary sate is attained, which is due to the formation of a tin precipitate near the membrane/solution interface as a consequence of the OH^- generated in the water splitting process. Tanaka et al. [26] reported that water dissociation can take place on cation-exchange membranes placed in divalent metallic chloride such as $MgCl_2$, $NiCl_2$ or $CoCl_2$. In these cases, the water dissociation is promoted when the corresponding metallic hydroxides are placed under the conditions of low ionic concentration and high electrical potential.

When the HCl is increased up to 0.1 M (Fig. 3), the increase of E_m observed after a short-time plateau coincides with the appearance of a precipitate of $Sn(OH)_2$ located at the anodic solution–membrane interface. This precipitate was observed for every HCl concentration under study. As mentioned previously, the E_m decrease after passing the maximum is a consequence of the higher mobility of protons that cross the CEM. However, the maximum of E_m is less pronounced than that observed at lower HCl concentration (Fig. 2), since the protons responsible for its appearance are already in solution, and the contribution of the H^+ generated as a consequence of water splitting is lower.

The transport of tetravalent cations, such as Sn(IV), through ion-exchange membranes submitted to an electric field is a complex phenomenon due to their high charge density leading to an important hydration shell, to their low mobility and, particularly, to their trend to form insoluble salts. Besides, Sn(IV) presents a high tendency to form hydroxylated complex species at moderate pH values [9,10] that can also compete for mass transport through the CEM.

The chronopotentiograms obtained in the cation-exchange membrane for 0.01 M $SnCl_4$ when the HCl concentration is 10^{-2} M and 10^{-1} M are illustrated in Figs. 4 and 5, respectively. In the case of 10^{-2}M HCl (Fig. 4) the limiting current is reported to appear at about 160 mA, therefore all the chronopotentiometric curves represented in Fig. 4 show the inflection point characteristic of the transition time. If the applied current is allowed to increase up to the overlimiting region (above 200 mA) the water splitting phenomenon occurs. The H^+ ions formed due to water splitting cross the membrane whereas the OH^- ions remain in the anodic side of the cation-exchange membrane, leading to a increase of pH. This pH increase enhances the formation of a Sn(IV) gelatinous species, probably the $Sn(OH)_6^{2-}$ monomer, which can polymerise and remain adhered to the membrane surface, causing the increase of the membrane potential (E_m) observed in Fig. 4 for an applied current of 220 mA.

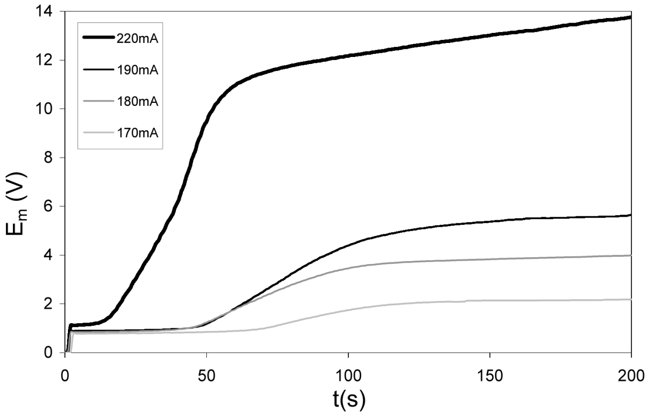

Fig. 4. Chronopotentiometric curves obtained in the CEM at different applied currents and for an electrolyte composed of 0.01 M $SnCl_4$ and 10^{-2} M HCl.

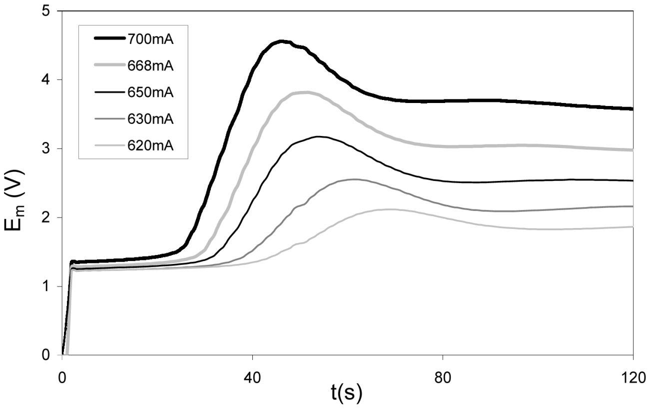

Fig. 5. Chronopotentiometric curves obtained in the CEM at different applied currents and for an electrolyte composed of 0.01 M $SnCl_4$ and 10^{-1}M HCl.

On the other hand, if the HCl concentration increases, the Sn(IV) gelatinous species adhered to the membrane could be re-dissolved as observed in Fig. 5 where the chronopotentiograms present a maximum characteristic of a precipitation/re-dissolution phenomenon, which can take place when the solution pH decreases.

4.2. Effect of hydrochloric acid on the transport of tin through the anion-exchange membrane (AEM)

The chronopotentiometric curves obtained in the anion-exchange membrane for 0.01 M $SnCl_2$ when the HCl concentration is 10^{-2} M and 10^{-1} M are presented in Figs. 6 and 7, respectively. In Fig. 6 well defined transition times for applied currents higher than the limiting value (around 20 mA) are obtained, and if the applied current belongs to the overlimiting region (above 30 mA), water splitting takes place producing OH^- and H^+ ions. For an applied current of 35 mA, E_m shows two slight plateaus. The first, at about 80 s, could be attributed to the Cl^- ions transport thought the membrane, whereas the second one, around 140 s, may be due to the transport of OH^- ions when chloride is completely depleted. This phenomenon only occurs for high values of the applied current.

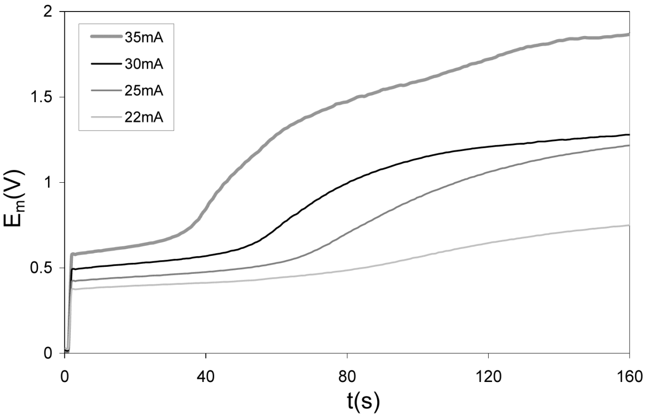

Fig. 6. Chronopotentiometric curves obtained in the AEM at different applied currents and for an electrolyte composed of 0.01 M $SnCl_2$ and 10^{-2} M HCl.

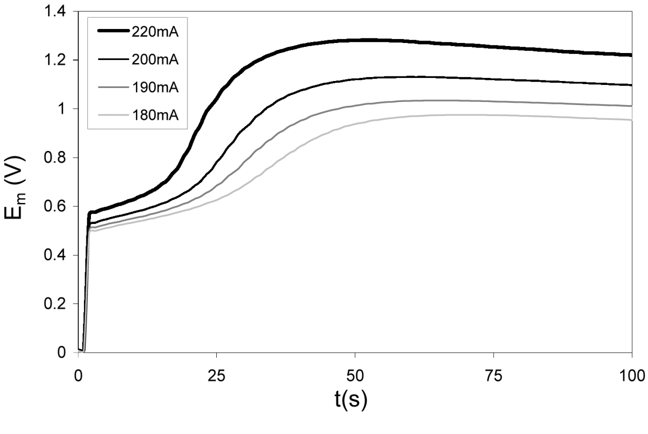

Fig. 7. Chronopotentiometric curves obtained in the AEM at different applied currents and for an electrolyte composed of 0.01 M $SnCl_2$ and 10^{-1} M HCl.

In the case of high HCl concentration (Fig. 7) a maximum of E_m in the chronopotentiometric curves is observed, and the steady state is achieved considerably later. Pimensakaia et al. [12] in a study of the behaviour of different anionic membranes attributed the potential decrease after passing the maximum to the following coupled effects of the concentration polarization: water splitting, electro-convection and gravitational convection at the membrane/diluted solution layer interface. The water spitting can diminish the electric resistance of the membrane due to appearing more mobile H^+ and OH^- ions. The electro-convection, which is defined as a non-gravitational convection caused by the interaction of a self-consistent electric-field with the corresponding electric charge of the membrane with sets the fluid in motion, can destroy partially the diffusion layer near the membrane and leads to a decrease of the membrane potential drop [27,28]. The role of electro-convection increases with decreasing the solution concentration and the diffusion layer thickness and the gravitational convection acts an important role in systems with large distance between the membranes and relatively high electrolyte concentration.

Therefore, for the experimental conditions presented in Fig. 7 and according to the study of Pimensakaia et al. [12], the decrease of E_m may be attributed to a combination of the higher mobility of the hydroxyl ions produced during the water splitting phenomenon with the gravitational convection occurring at these high concentrations and applied currents.

The chronopotentiograms obtained in the anion-exchange membrane for 0.01 M $SnCl_4$ when the HCl concentration is 10^{-3} M and 10^{-1} M are illustrated in Figs. 8 and 9, respectively. The last section of these chronopotentiometric curves of Fig. 8, when the current is switched-off, presents a characteristic diffusion relaxation behaviour similar to that found by Wilhem et al. [17] for bipolar membranes. According to these authors, for a monopolar ion-exchange membrane, when the current is switched-off the electric potential decrease to low values is very fast due to the relaxation of the concentration profiles in the solution boundary layer. For bipolar ion-exchange membranes directly after switching-off, the potential immediately drops to a plateau value. This plateau extends over longer times with higher current intensities as shown in Fig. 8. This is a result of the hindered recombination of hydroxide ions and protons in the bipolar interface. The reaction of OH^- ions and protons in the bipolar interface acts as a driving force for the diffusion of these ions within the respective membrane layer. The maximum negative slope of the electric potential in

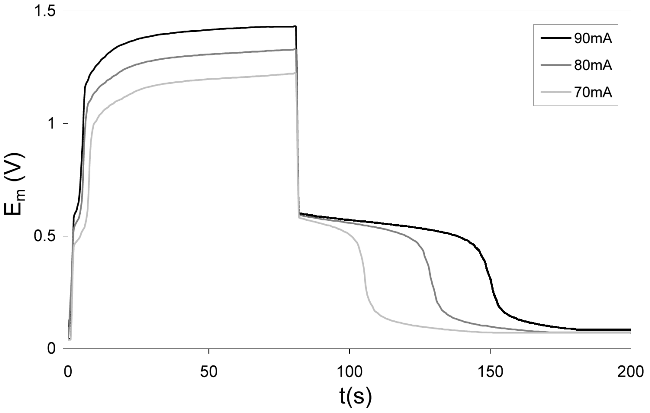

Fig. 8. Chronopotentiometric curves obtained in the AEM at different applied currents and for an electrolyte composed of 0.01 M $SnCl_4$ and 10^{-3} M HCl.

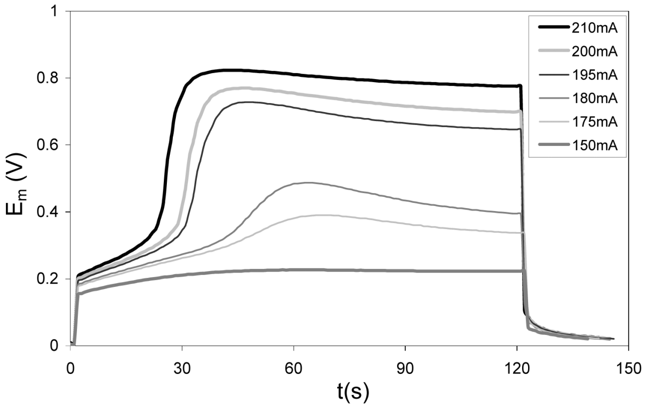

Fig. 9. Chronopotentiometric curves obtained in the AEM at different applied currents and for an electrolyte composed of 0.01 M $SnCl_4$ and 10^{-1}M HCl.

time indicates the discharging time of the membrane [29]. This same behaviour characteristic of bipolar membranes has also been obtained when the HCl concentration was 10^{-2} M HCl (not shown).

Water splitting, taking place at the membrane/solution interface, possibly causes the formation of insoluble metallic residues on the membrane surface. The metal hydroxides function as a resistive factor for ion transfer and their morphological structure or particle sizes may affect the ionic transport properties of the membrane. This fact causes a decrease in the net surface charge density by the formation of a bipolar structure, including H^+- and OH^--affinity groups on the membrane surface [30]. The formation of a bipolar structure enhances the water splitting capability because the H^+- and OH^--affinity groups prepolarize the water molecules at the solution-membrane interface. Similar behaviour was found by Kang et al. [31] and by Jialin et al. [30].

Fig. 9 presents the experimental results obtained when the HCl concentration is higher. If the applied current is higher than the limiting value, water splitting becomes important. However, the absence of any precipitate at this low pH explains the lack of the plateau in the diffusion relaxation region (zone 6 in Fig. 1). The OH^- ions formed due to water splitting are more mobile than chloride and are the species responsible for the decrease of E_m after the maximum observed in Fig. 9. For applied currents lower than the limiting value (150 mA) no maximum of E_m is observed as Cl^- ions are the only species capable of crossing the membrane.

5. Conclusions

This work presents a study of the transport properties of two ion-exchange membranes present in an electrochemical reactor used to process the wasted and rinse baths of the electroless plating of polymers industry. These baths are composed of tin as a major species, and hydrochloric acid in a concentration range that can vary depending on the nature of the bath, i.e. concentrated or diluted baths. In this context, the influence of the hydrochloric acid on the transport properties of tin through both cation-and anion- exchange membranes has been evaluated by chronopotentiometry.

The shape of the chronopotentiograms depends on the species under consideration, Sn(II) or Sn(IV), the hydrochloric acid concentration and the type of membrane. In the case of the study of Sn(II) transfer through the cation-exchange membrane, the contribution of the water splitting is evident for every hydrochloric acid concentration by the increase of the membrane potential after a short-time plateau observed in the chronopotentiograms, and by the appearance of a $Sn(OH)_2$ precipitate located at the anodic solution-membrane interface. The transport of Sn(IV) through the cation-exchange membranes is a complex phenomenon due to its high charge density leading to an important hydration shell, to its low mobility and, particularly, to its trend to form hydroxylated complex species and insoluble salts. In this case, low HCl concentration and high applied currents leads to the formation of a Sn(IV) species, probably the $Sn(OH)_6^{2-}$ monomer, which can polymerise and remain adhered to the membrane surface. This species is re-dissolved when the HCl concentration is increased.

In the case of Sn(II) transfer through the anion-exchange membrane, if the applied current is high and the HCl concentration is low, the OH^- ions produced due to water splitting are forced to cross the membrane when the chloride concentration in solution is depleted. For higher HCl concentration, the decrease in the membrane potential after the peak observed in the chronopotentiograms is due to the development of the gravitational convection phenomenon which is coupled with the water splitting at those high applied currents. The presence of

Sn(IV) at low HCl concentration in the overlimiting region produces a diffusion-relaxation region characteristic of the bipolar membranes. On the other hand, at lower pH values the formation of any Sn(IV) precipitate is avoided, and the OH^- ions formed during water splitting are the species responsible for the decrease of E_m after the peak observed for applied currents higher than the limiting value. This fact is due to the higher mobility of OH^- ions in comparison with chloride.

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