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Evaluation of the transport properties of copper ions through a heterogeneous ion-exchange membrane in etidronic acid solutions by chronopotentiometry

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ABSTRACT

The transport properties of copper chelates across an anion-exchange membrane were investigated by means of chronopotentiometry. Several solutions containing etidronic acid, copper sulfate and potassium chloride were evaluated. Tests were accomplished in a three-compartment reactor using a heterogeneous membrane containing quaternary ammonium functional groups. Results showed a strong relation between the amount of chelated anions and the limiting current density, the electrical resistance and the concentration polarization. An increase in the anionic equivalent charge of the solutions modified the three regions of the current-voltage curves. The acid medium was found to be less favorable because of the possibility of the formation of non-charged species in overlimiting regions. The presence of chloride anions increased the limiting current density, especially when the chloride concentration exceeded the etidronic acid concentration.

1. Introduction

The transport of ions across ion-exchange membranes has been widely studied since it can involve complex interactions between counter ions and fixed functional groups for a given current density regime. Throughout the last years, many researches have been developed in order to describe ion transport properties in several electrodialysis applications. Special attention has been given to the effects of membrane heterogeneity, to the improvement of membrane performance, to mass transfer enhancement in overlimiting regimes, to the influence of different electrolytes in the transport of transition metals and to the effect of complex formation in the transfer properties [1–13].

The study of ion transport through semipermeable membranes is often performed with the aid of chronopotentiometry, a classical electrochemical characterization method that measures the potential difference of a system in response of an imposed current density [14,15]. One of the most important advantages of chronopotentiometry for membrane systems is the possibility of measuring the dynamic potential drop response as a function of time which can provide more detailed information on non-steady transport state in the membrane

and in the adjacent solution layers. The obtained response allows the evaluation of the transport phenomena at the membrane-electrolyte interface. Thus, chronopotentiometry has been applied as a complementary tool in studies involving electrodialysis membranes. The formation of poisonous compounds at specific conditions [16], the analysis of fouling potential in membranes [17,18], the occurrence of overlimiting mechanisms such as gravitational convection or electroconvection [15] are some examples of chronopotentiometry applied for understanding transfer mechanisms in electrodialysis systems.

Chronopotentiometry applied to ion-exchange membrane systems is based on a typical description of a membrane-electrolyte interface recognized by many authors [6,19–21], as shown in Fig. 1.

According to the classical Sand theory, when a current density is applied to the system, a non-steady state starts at the instant of the perturbation and develops until the statement of a steady-state. During the non-steady state, the flux of counterions inside the membrane is governed by electromigration while the flux of counterions in the diffusion boundary layer is governed by a combination of diffusion and electromigration mechanisms. If that the counterion concentration C at the membrane surface varies throughout time as a function of the
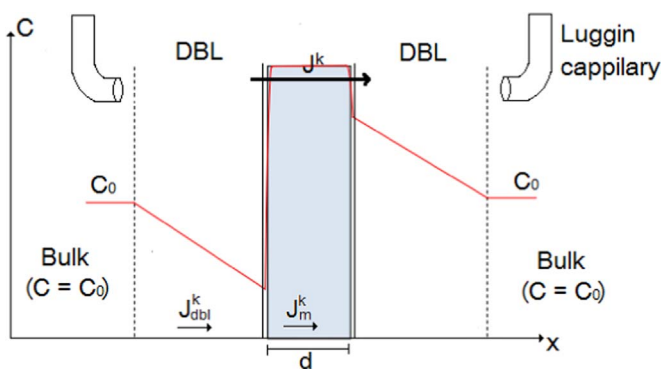
Fig. 1. Scheme of a membrane-electrolyte interface (adapted from [19,20]). C is the counterion concentration, C_0 is the counterion concentration at the initial condition and d is the membrane thickness. J^k is the flux of counterions. J^k_m and J^k_{bdl} represent the fluxes of counterions inside the membrane and in the DBL, respectively.

applied current density, it may be assumed that C decreases with time following the second Fick's law. The suitable boundary conditions assumed for Sand theory are: the existence of an interface between an ion-selective surface and an electrolyte solution; the membrane presents a homogeneous surface; there is lack of turbulence (which could promote convection). By assuming the latter, it is also assumed an unlimited growth of the diffusion layer, and an ion transport controlled by semi-infinite diffusion [14,15,22]. For the established conditions, the second Fick's law can be solved by using a Laplace transformation [22], resulting in the classical Sand equation (Eq. (1)).

$$\tau = \frac{\pi . D}{4} \left(\frac{C_0 . z . F}{\bar{t_j} - t_j} \right)^2 . \frac{1}{i^2} \tag{1}$$

In Eq. (1), τ is the so-called "transition time", defined as the time elapsed until the depletion of counterions in the diffusion boundary layer. D is the electrolyte diffusion coefficient, C_0 is the electrolyte concentration at $t = 0$ s, z is the counterion charge, F is the Faraday constant, i is the applied current density, $\bar{t_j}$ and t_j are the counterion transport numbers in the membrane and in the solution, respectively.

For the established conditions, the chronopotentiometric curves present a characteristic shape exhibited in several studies [14,15,22] (Fig. 2).

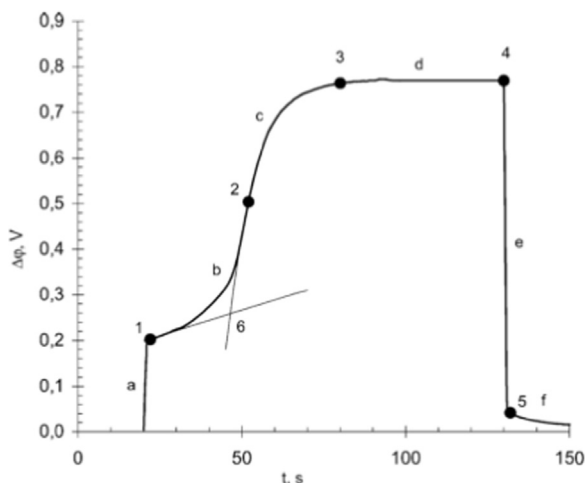A typical chronopotentiometric arrangement for studying mem-

Fig. 2. Characteristic shape of a chronopotentiometric curve obtained for a monopolar ion-exchange membrane [15]. The inflexion point (point 6) represents the transition time (τ). Point 1 is the potential drop due to the application of a given current density. Point 2 is due to the depletion of counterions in the DBL. Point 3 represents the achievement of the steady-state. Point 4 is the interruption of electric current. Point 5 presents the relaxation of the system. Note that, when $i < i_{lim}$, chronopotentiograms do not present any inflexion point.
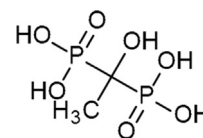

Fig. 3. Structural formulae of etidronic acid (H_4HEDP) [24].

brane systems consists in a four-electrode assemblage in which one reference electrode is positioned near each of the membrane-electrolyte interfaces. The potential response between the reference electrodes is registered while a current density is applied between the working electrode and the counter electrode. The shape of the chronopotentiometric curves provides information regarding to the parameters related to ion transport across the membrane, i.e., the limiting current density, the electrical resistance, the effect of overlimiting transport mechanisms and the transport number of an ion [19,23].

In the present work, chronopotentiometry was used to investigate the transport properties of copper chelates across an anion exchange membrane. The evaluated chelating agent was 1-hydroxyethane-1,1-diphosphonic acid (HEDP or etidronic acid). The etidronic acid is an organophosphonate used as chelating agent mostly for industrial cleaning applications. It is produced from the reaction between phosphorus trichloride (PCl_3) and acetic acid (CH_3COOH), resulting in a bisphosphonate having its molecular structure as presented in Fig. 3 [24].

Etidronic acid has been evaluated as a less toxic alternative for cyanide in plating baths [25–27]. A HEDP-based alkaline strike bath for copper plating on Zamak substrates in barrel plating systems was developed by the Institute for Technological Research, in Brazil [26]. As a result, a suitable bath was produced and the electrodeposited copper coats exhibited adherence and visual aspect comparable with cyanide-based baths. It is important to mention that the main characteristic of a strike bath is its ability to form stable metal complexes and decrease the Me^{z+} reduction potential. Strike baths are utilized to perform metal deposition as undercoats to prevent the lack of adherence caused by galvanic deposition. According to the literature [26,28,29], the most probable cupric [CuHEDP] chelates to be formed are $[CuHEDP]^{2-}$, $[CuHHEDP]^-$ and $[CuH_2HEDP]$. In alkaline solutions (pH > 7), $[CuHEDP]^{2-}$ is the prevailing found specie [28].

A previous study [30] evaluated electrodialysis (ED) as an alternative for treating synthetic wastewaters from the mentioned HEDP-copper bath. Percent extraction up to 99.7% of copper ions and 94.4% of HEDP were obtained, indicating that electrodialysis may be an alternative for treating HEDP-based solutions. The study also showed that, for synthetic wastewaters with pH higher than 5.4, copper ions were transferred to the anodic side of the ED system, in accordance with the anionic chelate formation theory. Nevertheless, no clogging in anionic membranes was observed [30].

Due to the formation of stable anionic cupric chelates observed previously, the present work proposes a detailed investigation on the transport properties of [CuHEDP] chelates through an anion exchange membrane using chronopotentiometry. The effect of the HEDP:Cu^{2+} ratio was evaluated by using several solutions having ion concentration similar to the synthetic rinsing waters from the strike copper bath. The influence of pH and of potassium chloride addition was also investigated.

2. Experimental

2.1. Working solutions

The study was carried out using solutions containing copper (II) sulfate pentahydrate ($CuSO_4 \cdot 5H_2O$), etidronic acid (HEDP) and potassium chloride (KCl) in different concentrations. The evaluated solutions were originated from a model wastewater based on the abovemen-