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Electrochemistry of 2,8-dithia[9],(2,9)-1,10-phenanthrolinophane (L) at the polarized water/1,2-dichloroethane interface: Evaluation of the complexation properties towards transition and *post*-transition metal ions

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Abstract

The coordination chemistry of 2,8-dithia[9],(2,9)-1,10-phenanthrolinophane (**L**) towards transition and *post*-transition metal ions such as Cu(II), Cu(I), Cd(II), Co(II), Ni(II), Pb(II) and Zn(II) was studied at the polarized water/1,2-dichloroethane interface by cyclic voltammetry. The dependence of the half-wave transfer potential on the ligand and metal concentrations was used to formulate the stoichiometry, and to evaluate the association constants of the complexes formed between **L** and Pb(II).

Keywords: Phenanthroline derivatives; Liquid|liquid Interfaces; Complex formation; Metal ion electroassisted transfer; ITIES

1. Introduction

The quest for new macrocyclic ligands capable of specific molecular recognition of metal ions is a topic of current interest both to analytical chemistry and separation science [1–3]. Since 1979 when Koryta [4] demonstrated the assisted transfer of metal ions at polarized interfaces between two immiscible electrolyte solutions (ITIES), this methodology has developed into a powerful alternative to more traditional procedures used for complex characterization, allowing a deeper insight into the interactions between ligands and metals [5–9], and a better understanding of the role played by the solvent and pH in the complex stability [10,11]. Although the earlier studies on the assisted ion transfer at ITIES were focused on group I and group II ions [4], soon they were extended to transition and heavy-metal ions [12–14]. In this respect, phenanthroline derivatives represented the first choice as ligands, see the work by Wang and Lin [15] for the assisted transfer of Ni(II) and Co(II), Yoshida and Freiser [12] for the assisted transfer of Cd(II), Zn(II), Co(II) and Ni(II), Doe et al. [16] for the assisted transfer of Cu(II) as 1,10-phenanthrolinetrifluoroacetylacetone complex, Dassie et al. [17] for Ca(II), Sr(II) and Mg(II), Fernández et al. [18] for the assisted transfer of Mg(II). Furthermore, Sanchez et al. [19] used theoretical calculations to explain the ordering of the Gibbs energies for the assisted transfer across the water/1,2-dichloroethane interface of Li(I), Na(I), and K(I) complexes with 1,10-phenanthroline. In fact, beside a theoretical framework for the determination of parameters such as

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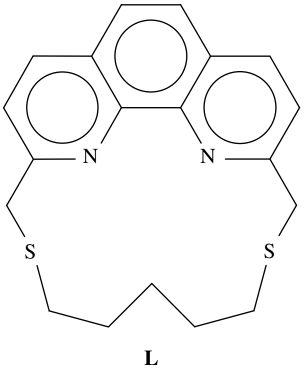
the stoichiometry of the complexes involved in the transfer process [4–10], a very important step in this field was the development of effective tools to evaluate the Gibbs energy for the transfer of very hydrophilic ions such as transition metal ions [20,21].

Recently, we have reported the synthesis and the coordination properties towards transition and *post*-transition metal ions of new mixed aza-thioether crowns containing the 1,10-phenanthroline (phen) unit as an integral part of the macrocyclic structure [22–27]. These ligands have shown a great affinity for transition metal ions such as Pb(II), Cd(II), Hg(II) [24] as well as Ni(II), Pd(II), Pt(II), Rh(III), Ru(II) [22,23,25], Ag(I) [26], Cu(II) [27], with coordination properties strictly dependent upon the conformational constraints imposed by the heteroaromatic moiety on the S-donor thioether linker of the ring. Furthermore, some of these new macrocyclic ligands have also been used as neutral ionophores for the construction of ion-selective membrane electrodes for Ag(I) [28] and Cu(II) [29], and in the case of 2,5,8-trithia[9],(2,9)-1,10-phenanthrolinophane the coordination chemistry towards Rh(III) at the polarized water/1,2-DCE interface was also studied [30]. Herein we report the study by cyclic voltammetry of the assisted transfer of Cu(II), Cu(I), Cd(II), Co(II), Ni(II), Pb(II), and Zn(II) by interfacial complexation with 2,8-dithia[9],(2,9)-1,10-phenanthrolinophane (**L**) at the polarized water/1,2-dichloroethane interface. The experimental results and data interpretation leading to the complexes characterization and to the evaluation of the association constants will be presented and discussed.

2. Experimental

2.1. Chemicals

The organic electrolyte salts used in this study were tetraoctylammonium tetrakis(phenyl)borate (TOATPB) prepared as reported previously [31] and the bis(triphenylphosphoranylidene) ammonium tetrakis(4-chlorophenyl)borate (BTPPATPBCl) which was prepared by the metathesis of BTPPACl (Aldrich) and KTPBCl (Fluka). 2,8-Dithia[9],(2,9)-1,10-phenanthrolinophane (**L**), represented in Scheme 1, was synthesized according to a procedure described elsewhere [24]. *n*-Tetraalkylammonium chlorides (TEACl, TMACl and TPrACl) from Aldrich were used as reference ions in the aqueous phase. LiCl (>99% purity) and metal chlorides (p.a.) were obtained from Merck, acetic acid (>99% purity), sodium acetate, p.a. Merck. Aqueous solutions were prepared with purified water from Milli-Q system (Millipore) with 18 MΩ · cm resistivity. 1,2-Dichloroethane (1,2-DCE) (>99.5% purity, Merck) was used without further purification and was handled with all necessary precautions.



L

Scheme 1.

2.2. Electrochemical measurements

Cyclic voltammetry was performed using a four electrode potentiostat (Solartron 1287) with ohmic drop compensation. The electrochemical cell was made from borosilicate glass and it was of the same design as used previously [21] with two Luggin capillaries probes and geometrical area for the water/1,2-DCE interface of 0.28 cm^2. All the measurements were carried out at laboratory temperature (20 ± 3 °C), with scan rate ranging from 10 to 100 mV/s. For each experiment predetermined addition of TEA^+, TMA^+ or $TPrA^+$ provided a reference for all half-wave potential measurements. The selection of the tetraalkylcation was made accordingly to the transfer potential of the metal complex in order to avoid superposition of both voltammetric waves. The values measured were transposed to the Galvani potential scale taking into account the following relationship:

$$E_{1/2} - \Delta_{\mathrm{o}}^{\mathrm{w}}\phi^0 = E_{1/2}(\mathrm{TAA}^+) - \Delta_{\mathrm{o}}^{\mathrm{w}}\phi^0(\mathrm{TAA}^+), \qquad (1)$$

where $\Delta_{\mathrm{o}}^{\mathrm{w}}\phi^0(\mathrm{TAA}^+)$ represents the value of the transfer potential of tetraalkylammonium ions ($TPrA^+$, TEA^+, TMA^+). We have used the value of $\Delta_{\mathrm{o}}^{\mathrm{w}}\phi^0(\mathrm{TMA}^+), = 160$ mV as reference for our measurements [32].

3. Results and discussion

The evaluation of the thermodynamic properties of the complexes under study requires the definition of a correct potential scale and therefore this is a critical step for any further calculations which can be performed. The choice of the appropriate ions to establish the potential scale will also depend on the potential of transfer of the complexes that are being studied in order to assure that it is possible to carry on measurements where both complex and reference ions can be easily distinguished when both are present in the electrochemical cell. Fig. 1 shows a cyclic voltammogram obtained for the simultaneous transfer of three tetraalkylammonium ions (tetrapropylammonium, tetraethylammonium and tetramethylammonium) from the aqueous to the organic phase.

From the analysis of this figure it is possible to extract the peak to peak separation between the different ions. In the present case the differences between the transfer potential for $TPrA^+$, TEA^+ and TMA^+ are presented in Table 1.