

Design of redox systems for the transport of electrons across liquid membranes: Poly-aza-macrocyclic metal complexes

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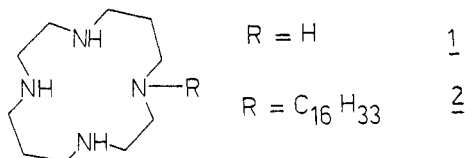
Abstract - The design of a novel carrier able to perform selective electron transport across liquid membranes is described. The three-phase device allows to oxidize metal centred redox agents with aqueous peroxydisulfate. With the help of a kinetic control the device makes the very strong and non-selective oxidizing agent peroxydisulfate to discriminate amongst a mixture of different reducing agents of varying power.

INTRODUCTION

Electrons can be transported from an aqueous reducing layer (Electron Source Phase, ESP) to an aqueous oxidizing layer (Electron Receiving Phase, ERP) across a liquid membrane, which contains an appropriate redox system acting as an electron carrier. The membrane can be a water immiscible liquid which impregnates a porous film (supported liquid membrane) or a layer which interfaces two aqueous solutions of comparable volume (bulk liquid membrane).

Very few investigations have been devoted to electron transport experiments across liquid membranes, in contrast to the thousands of articles on the transport of metal ions (in particular of the s block) mediated by synthetic macrocycles. The reported electron transport experiments were involved with the design of the experiment and were essentially intended to define the factors contributing to the driving force of the process.¹⁻⁴

In our laboratory experiments are currently being carried out to design novel carriers able to perform selective electron transport. In particular, the redox system in the membrane should be able to discriminate among aqueous mixtures of reducing agents (in ESP) and of oxidizing agents (in ERP) and to promote the development of selected oxidation and reduction processes. Hopefully, such a function should be regulated through an external control on the potential of the redox system used as a carrier. One hundred years of coordination chemistry has shown that substantial changes in the redox activity of metal ions can be generated through interaction with appropriate ligands. Thus, our attention has been addressed to transition metal centered redox carriers, whose one-electron redox changes, and corresponding electrode potentials, could be modulated through modifications of the coordinating environment.



NICKEL(II, III) REDOX CHANGE INSIDE THE CYCLAM FRAMEWORK

It is well known that incorporation of a divalent 3d cation in a tetra-aza macrocyclic ring makes especially easy the attainment of the higher oxidation state.⁵ This results from the ability of the cyclic ligand to establish very strong in-plane coordinative interactions, which raise the energy of the anti-bonding orbital, essentially metallic in character, from which the electron has to be abstracted in the oxidation process. The 14-membered fully saturated macrocycle (1), cyclam, is very effective in that and, for instance, allows the Ni(II)/Ni(III) redox change to occur at a moderate potential, in aqueous solution. Solid trivalent nickel cyclam complexes can be isolated as solids, through oxidation with peroxydisulfate in acidic solution. The [Ni(cyclam)SO₄]ClO₄ complex persists indefinitely in 1M H₂SO₄ and we have recently realized that in that medium it can be used as standard oxidizing

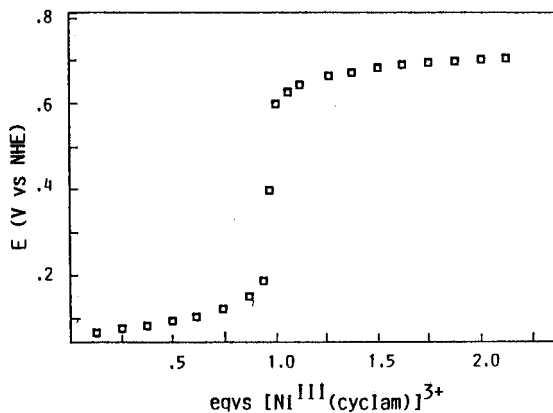


Fig. 1. Potential vs. equivalents of titrant added curve, for an experiment in which TiCl_3 , in 1M H_2SO_4 soln, is titrated with a standard soln of $[\text{Ni}^{\text{III}}(\text{cyclam})\text{SO}_4]\text{ClO}_4$ in 1M H_2SO_4 .

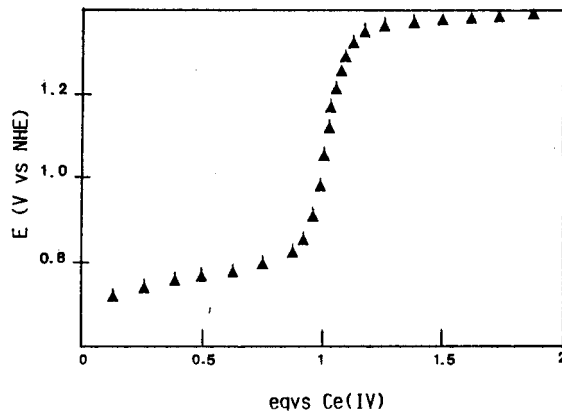


Fig. 2. Potential vs. equivalents of titrant added curve, for an experiment in which $[\text{Ni}^{\text{II}}(\text{cyclam})](\text{ClO}_4)_2$, in 1M H_2SO_4 soln, is titrated with a standard soln of Ce(IV) in 1M H_2SO_4 .

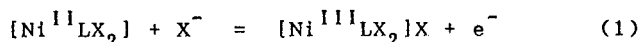
agent to oxidize conventional cationic reducing agents such as: Sn(II), Ti(III), Cr(II). As an example, Fig. 1 displays a typically S-shaped potential vs eqvs profile obtained by titrating a solution of Ti(III) with a standard solution of $[\text{Ni}^{\text{III}}(\text{cyclam})\text{SO}_4]\text{ClO}_4$, 1M in H_2SO_4 . On the other hand, the divalent complex, e.g. $\text{Ni}(\text{cyclam})(\text{ClO}_4)_2$, behaves as a reducing agent, being able to react, in acidic solution, with conventional oxidizing agents such as Ce(IV). The corresponding titration curve is shown in Fig. 2.

The above unusual behavior demonstrates the unique versatility of the Ni(III)/Ni(II) redox change inside the cyclam framework and designates it as a candidate for use as a carrier in the transport of electrons across liquid membranes.

N-CETYLCYCLAM: A LIPOPHILIC VERSION OF CYCLAM WHICH ANCHORS Ni(II)/Ni(III) REDOX COUPLE TO THE ORGANIC PHASE

An essential requirement for a redox system to act as an electron carrier across liquid membranes is the solubility in the organic phase (the membrane) and the complete insolubility in the aqueous phases. In this connection, the novel macrocycle 2 (N-cetylcyclam, L) in which a C_{16} aliphatic chain has been appended to a nitrogen atom of the cyclam ring, has been prepared through reaction of $\text{C}_{16}\text{H}_{33}\text{Br}$ with a five-fold excess of cyclam. N-cetylcyclam reacts with NiX_2 salts to give $[\text{Ni}^{\text{II}}\text{LX}_2]$ complexes soluble in the most common organic media (benzene, chloroform, dichloromethane). The hypothesized stereochemical arrangement for the above complexes is a more or less axially distorted octahedron, in which the macrocycle is equatorially chelated and the X^- anions occupy the apical sites. Noteworthy, the spin state of the metal centre, either in the solid state and in solution, depends upon the coordinative tendencies of the inorganic anions. Fairly coordinating anions, such as chloride, stabilize the high-spin form, blue in color; poorly coordinating anions, such as perchlorate, stabilize the low spin form, yellow in color.

Cyclic voltammetry experiments on dichloromethane solutions of $[\text{Ni}^{\text{II}}\text{LX}_2]$ complexes, made 0.1M in Bu_4NX , have shown that the metal centre undergoes a reversible one-electron oxidation process, which is assigned to the following redox change:



The half-wave potential values associated to half-reaction (1) depend strongly upon the nature of X and in particular upon its coordinating tendencies: donating anions (e.g. chloride) favor the access to trivalent species to a larger extent than poorly donating anions (e.g. perchlorate). The anion effect on the potential is spectacular ($\text{X} = \text{Cl}$: 0.175 V vs the Fc/Fc internal reference couple, $\text{X} = \text{ClO}_4$: 0.920 V) and may open the way to a thermodynamic control on the redox activity of the present system, chosen as an electron carrier.

The $[\text{Ni}^{\text{III}}\text{ClCl}_2]\text{Cl}$ species can be generated in bulk concentration through oxidation with chlorine of a CH_2Cl_2 solution of the corresponding divalent complex. The ESR spectrum of the frozen solution displays axial symmetry, with

the g_{\perp} value considerably greater than g_{\parallel} ; this is consistent with the formation of an authentic Ni^{III} cation, d^7 low-spin, in an elongated octahedral coordinative environment. Moreover, the g_{\parallel} feature is split into seven lines, which indicates the presence of two equivalent chlorine atoms in the axial positions of the elongated octahedron.

TWO-PHASE REDOX EXPERIMENTS: OXIDATION OF REDUCED FORM OF THE CARRIER BY AQUEOUS PEROXYDISULFATE

In order to assess the appropriate conditions to perform the three-phase (electron transport) experiment, two-phase redox processes have been preliminarily investigated, which involve: (i) the oxidation of the $[Ni^{II}LX_2]$ complex in CH_2Cl_2 by an aqueous oxidizing agent, at one side of the membrane, and (ii) the reduction of the oxidized complex, $[Ni^{III}LX_2]X$, by an aqueous reducing agent, at the other side.

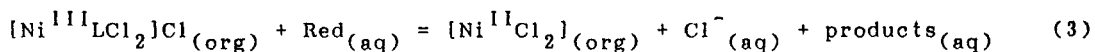
As far as carrier oxidation experiments are concerned, the peroxydisulfate ion was tested as an oxidizing agent, and an aqueous layer 0.1M in $Na_2S_2O_8$ and 1M in NaX was equilibrated with a dichloromethane layer of $[Ni^{II}LX_2]$. The investigated reaction is described by the following equation:



When $X = Cl$, the pale violet organic layer takes an intense bright yellow color, due to the oxidation of the divalent species to the $[Ni^{III}LCl_2]Cl$ complex. On the other hand, when $X = ClO_4$, no color change occurs and reaction (2) does not take place. This behavior should be ascribed to the strikingly different reducing properties of the $[Ni^{II}LCl_2]$ and $[Ni^{II}L(ClO_4)_2]$ complexes. In particular, electrochemical investigations in CH_2Cl_2 , described in the previous paragraph, have shown that the potential associated to the Ni^{III}/Ni^{II} redox couple for the chloride complex is much less positive than that observed for the perchlorate complex. Thus, trying to juxtapose the electrochemical scale in water and that in dichloromethane, the reduction potential of aqueous peroxydisulfate (1.96 V vs NHE) should be set above that for the $[Ni^{III}LCl_2]Cl/[Ni^{II}LCl_2]$ redox couple, but below that of the $[Ni^{III}L(ClO_4)_2]ClO_4/[Ni^{II}L(ClO_4)_2]$ redox couple in dichloromethane solution.

TWO-PHASE REDOX EXPERIMENTS: REDUCTION OF OXIDIZED FORM OF THE CARRIER BY AQUEOUS REDUCING AGENTS

Conventional aqueous reducing agents were tested for the reduction of the $[Ni^{III}LCl_2]Cl$ complex in CH_2Cl_2 , through two-phase experiments. Metal centered reducing agents such as $Fe(II)$, $Ti(III)$ and $Cr(II)$, in aqueous 1M HCl, are able to reduce the oxidized form of the carrier; the same is done by the metal cage complex: $[Co^{II}(diarsarH_2)]^{4+}$. The two-phase redox process can be described by the following reaction:



Interestingly, when the CH_2Cl_2 layer containing the $[Ni^{III}LCl_2]Cl$ complex is equilibrated with an aqueous solution 0.1M in NaI and 1M NaCl, reaction (3) does not take place. The reason of this behavior cannot be thermodynamic since iodide is a stronger reducing agent (0.54 V vs NHE) than $Fe(II)$ (0.77 V vs NHE), which reduces $[Ni^{III}LCl_2]Cl$ under two-phase conditions. On the other hand, it should be noted that reduction of $[Ni^{III}LCl_2]Cl$ by I^- takes place under single-phase conditions. In fact, the $[Ni^{III}LCl_2]Cl$ complex in CH_2Cl_2 solution is instantaneously reduced on addition of a CH_2Cl_2 solution of Bu_4NI . Moreover, the two-phase reduction takes place if the aqueous layer is not charged with NaCl, but contains only 0.1M NaI. It seems probable that, as a first step, an exchange of Cl^- ions (from the CH_2Cl_2 layer) and I^- ions (from the aqueous layer) takes place, the iodide ions going to occupy the axial coordination sites of the Ni^{III} complex; then, as a second step, reduction of the trivalent metal centre occurs through an intramolecular mechanism, in single-phase conditions. Thus, aqueous chloride prevents the reduction of the Ni^{III} complex since it competes successfully with aqueous iodide for the transfer in the CH_2Cl_2 layer.

ELECTRON TRANSPORT EXPERIMENTS

On the basis of the two-phase redox processes described in the previous paragraphs, electron transport experiments across a liquid membrane, mediated by the $[Ni^{III}LCl_2]Cl/[Ni^{II}LCl_2]$ redox system, can be designed. Experiments

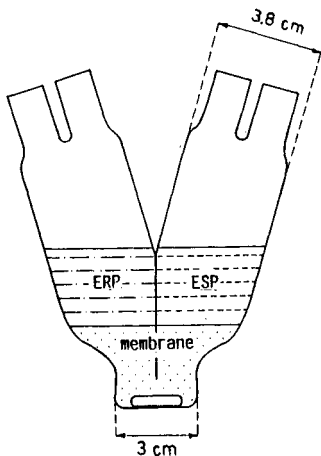


Fig. 3. Glass vessel used in electron transport experiments. The transfer of electrons from aqueous ESP (reducing compartment) to aqueous ERP (oxidizing compartment) is mediated by the metal centered redox system dissolved in the CH_2Cl_2 membrane.

were performed using the glass vessel drawn in Fig. 3, in which a CH_2Cl_2 bulk liquid membrane (25 cm^3) separates two aqueous layers: the Electron Receiving Phase, ERP, 25 cm^3 , 0.1M in $\text{Na}_2\text{S}_2\text{O}_8$ and 1M in NaCl , and the Electron Source Phase, ESP, 25 cm^3 , 0.01M in the reducing agent (Fe(II) , Ti(III) , Cr(II)) and $[\text{Co}^{\text{II}}(\text{diamsarH}_2)]^{4+}$ and 1M in HCl . The membrane was stirred magnetically and ESP and ERP layers were stirred by rotating glass rods, at a constant rate.

The course of the electron transport experiment can be followed visually. For instance, when Cr(II) is used as a reducing agent, at the beginning of the experiment the ESP solution has the pale blue color, due to the chromous ion, which, in a matter of minutes, turns green due to the oxidation to the trivalent state. The color change of ESP with the $[\text{Co}^{\text{II}}(\text{diamsarH}_2)]^{4+}$ reducing complex is even sharper: the solution turns from the olive-green color of the Co(II) cage complex to the bright orange color of the oxidized species (but, in this case the change takes hours to occur). The oxidation of the reducing agent in ESP can be monitored in a quantitative way through the potential of a platinum or a mercury electrode. From the potential values it is possible to calculate, through the Nernst equation, the percent concentration of the oxidized form in ESP. Plots of % values vs time (see Fig. 4) are S-shaped and fully describe the course of the electron transport experiments.

The mechanism of the electron transport process can be represented by the general Scheme outlined in Fig. 5: aqueous $\text{S}_2\text{O}_8^{2-}$ at the ERP/membrane interface oxidizes $[\text{Ni}^{\text{II}}\text{LCl}_2]$ to $[\text{Ni}^{\text{III}}\text{LCl}_2]\text{Cl}$ with simultaneous extraction of a Cl^- ion from ERP; then $[\text{Ni}^{\text{III}}\text{LCl}_2]\text{Cl}$ diffuses across the CH_2Cl_2 layer to the membrane /ESP interface, where it takes one electron from the aqueous reducing

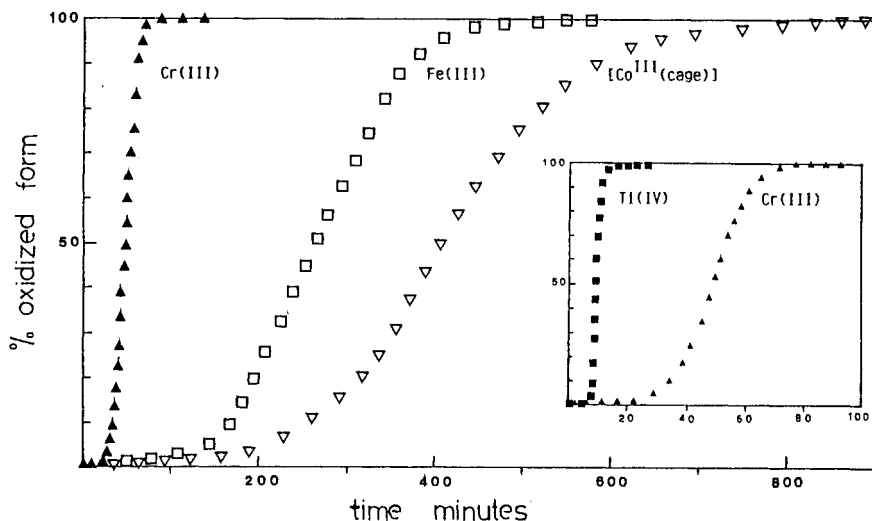


Fig. 4. % of the oxidized form of the reducing agent which forms in ESP during the electron transport experiment. % vs time profiles indicate that the time required for the electron transport to be complete ranges from a few minutes (reducing agent: Ti(III)) to several hours (reducing agent: $[\text{Co}^{\text{II}}(\text{cage})]$ complex).

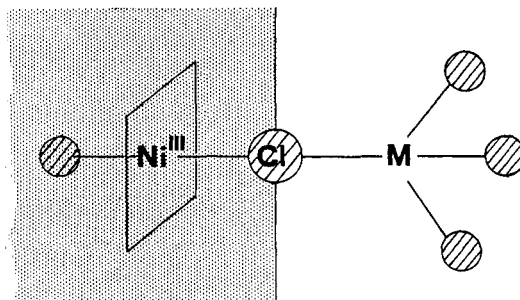
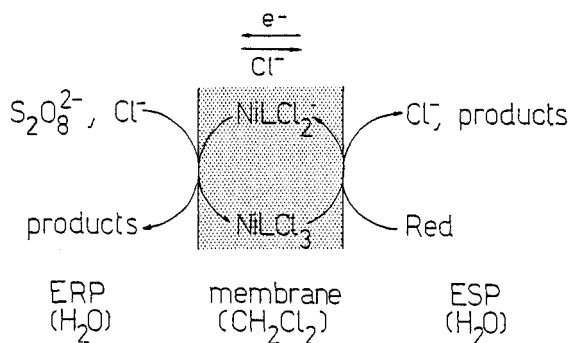
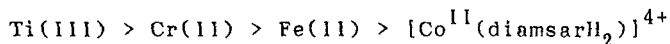


Fig. 5. Scheme describing the process by which electrons flow from the reducing compartment (ESP; Red = Fe(II), Ti(III), Cr(II), [Co^{II}(cage)]⁴⁺) to the oxidizing compartment (ERP). Chloride ions counterflow from ERP to ESP.

Fig. 6. Hypothesized mechanism for the electron transfer from a metal centered reducing agent to the oxidized form of the carrier, at the ESP/membrane interface. Electron transfer should occur via a Cl⁻ ion, bridging the reducing metal centre M and the Ni^{III} ion of the carrier.

agent and simultaneously releases a Cl⁻ ion. At this point, the reduced [Ni^{II}LCl₂] complex goes back to the other side of the membrane to start a new redox cycle. Shuttling of the carrier stops when all the reducing agent in ESP, the limiting reagent of the three-phase redox process, has been consumed. Considering that the [Ni^{II}LCl₂] complex in the membrane is 0.001M and the reducing agent in ESP is 0.010M, each carrier molecule has to do ten trips, back and forth, across the CH₂Cl₂ layer. On the whole, electrons are carried from ESP to ERP by [Ni^{II}LCl₂], whereas chloride ions are carried from ERP to ESP by [Ni^{II}LCl₂]Cl.

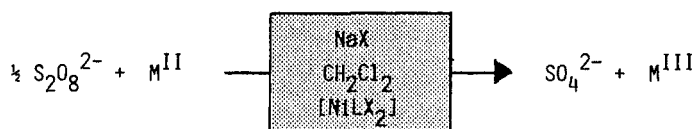
The really impressive aspect of the described experiments is the extremely variable rate at which the transport can take place, depending upon the nature of the reducing agent in ESP. In fact (see Fig. 4), the time required for the electron transport to be complete varies over a range from a few minutes (about ten for the fastest reducing agent: Ti(III)) to several hours (about twelve, for the slowest reducing agent employed: the [Co^{II}(cage)] complex). Figure 4 shows that the transport rate decreases according to the following sequence:



Notice that the above sequence does not correlate at all with redox potential values. It should be considered that the investigated metal centered reducing agents (except the [Co^{II}(cage)] complex) exist in aqueous 1M HCl as chloro-complexes or aquo-chloro-complexes. Therefore, it is possible that the electron transfer at the ESP/membrane interface takes place via a chloride ion bridging the Ni^{III} and the M metal centers (M= Ti(III), Fe(II), Cr(II); see Fig. 6). This hypothesized mechanism could account for the very slow electron transport observed when the [Co^{II}(diamsarH₂)]⁴⁺ complex is used as a reducing agent: the aliphatic framework of the sarcophagine ligand shields the Co^{II} center and prevents the formation of the chloride bridge. Thus, the electron transfer is forced to occur through a much slower outer-sphere mechanism.

CONCLUSIONS

In the present study we have developed a three-phase device that allows to oxidize metal centered redox agents with aqueous peroxydisulfate, according to the following scheme:



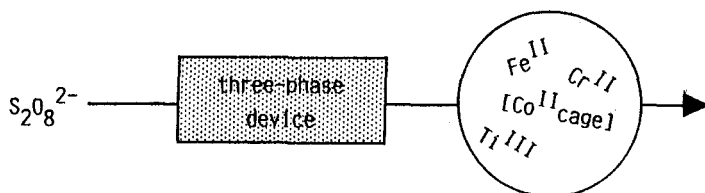
THREE-PHASE TREATMENT OF A CONVENTIONAL AQUEOUS REDOX PROCESS

THERMODYNAMIC CONTROL: appropriate choice of the background electrolyte NaX makes the process to occur or not to occur

KINETIC CONTROL: nature of the reducing agent determines the rate of the redox process (SELECTIVITY)

It should be noted that, even in the less favorable case (Red = Fe^{II}), a largely positive potential difference is associated to the above reaction, which is completely displaced to the right. In the presently investigated conditions, electron transfer from Red_(aq) to S₂O₈²⁻_(aq) does not take place directly, but is mediated by a carrier, the lipophilic Ni^{II} tetra-aza-macrocyclic complex, dissolved in the organic layer, which separates the two aqueous oxidizing and reducing compartments. It has been demonstrated that the course of the reaction can be controlled by charging the aqueous phase with an appropriate background electrolyte: NaCl activates the electron transport, since Cl⁻ ions, through axial coordination to the metal center of the carrier, stabilize enough the Ni^{III} state to allow the abstraction of one electron. On the other hand, ClO₄⁻ is too weak a donor to permit the formation of the Ni^{III} complex in the membrane, and neither oxidation by S₂O₈²⁻, nor electron transport occur. This can be considered a thermodynamic control, since the nature of the X⁻ anion modulates the potential of the redox system to be used as carrier, and switches on and off the electron transport process.

Most noteworthy, a kinetic control has also been discovered, which depends on the rate at which the chosen aqueous reducing agent releases electrons to the carrier at the ESP/membrane interface: this rate varies dramatically with the nature of the reducing agent. Due to this kinetic effect, the described three-phase device makes the very strong and non-selective oxidizing agent peroxydisulfate to discriminate among a mixture of different reducing agents of varying power. For instance, Fig. 4 indicates that oxidation of Ti(III) and Cr(II) is complete well before the oxidation of Fe(II) takes place to a significant extent. The discriminating ability of the S₂O₈²⁻ ion toward reducing agents, in the three-phase device, is illustrated by the following scheme:



The concept of selective oxidation and reduction processes through a three-phase device can be further developed through the design of novel lipophilic redox systems, whose potentials could be modulated, in order to cover a wider range. This type of approach could be especially useful in separation technology, where the controlled variation of their oxidation states can make much easier the selective extraction and recovery of metal ions in a mixture.

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