

Metal complexes that transport electrons across liquid membranes

Giancarlo De Santis, Antonio Poggi, Barbara Seghi, and Luigi Fabbrizzi*

Dipartimento di Chimica Generale, Università di Pavia, 27100 Pavia, Italy

Abstract Lipophilic metal complexes, displaying one electron redox activity, are used as carriers for the transport of electrons across bulk liquid membranes from an aqueous reducing phase to an aqueous oxidizing phase. The $[\text{Fe}^{\text{III,II}}(\text{bpy})_3]^{3+/2+}$ redox system (bpy = 4,4'-di-*tert*-butyl-2,2'-dipyridyl, **1**) transports electrons from both cationic and anionic aqueous reducing agents to aqueous Ce(IV) and counter-transporters perchlorate ions in the opposite direction. Electron/chloride ion cross transport between aqueous persulfate and aqueous metal centred reducing agents, mediated by the membrane dissolved $[\text{Ni}^{\text{II,III}}\text{LCl}_2]^{2+/3+}$ redox system (L = (*N*-cetyl)-cyclam, **2**) takes place at a much higher rate. The overall transport rate in the two types of experiments is controlled by that of the redox process occurring at the membrane/aqueous reducing phase interface and is to be related to the type of mechanism (*inner* or *outer sphere*) by which the two-phase electron transfer process takes place.

INTRODUCTION

A water immiscible liquid layer separating two aqueous layers behaves as a *membrane* if it contains a molecular system (*the carrier*) able to extract a substrate from one of the aqueous layers (*the source phase*, SP) and to release it to the other one (*the receiving phase*, RP). The carrier works in a cyclic way, shuttling back and forth between the two membrane/aqueous phase interfaces. Looking at the energy aspects, the process may be driven by a gradient of concentration of the substrate and in this case the three-phase system reaches its stationary state when substrate concentration is the same either in SP and RP. When the substrate is a metal salt MX_n , a lipophilic ligand L, able to complex M^{n+} , can be used as a carrier: the complex species $[\text{ML}]X_n$ travels across the membrane from SP to RP in a first trip and the uncomplexed carrier L moves from RP to SP in the trip back. Bonding features of the $[\text{ML}]^{n+}$ complex, in particular the capability of L to satisfy stereochemical requirements of M^{n+} , may generate selectivity, making liquid membranes promising tools in separation science and technology. Selective separation of salts of block s metal centres has been thoroughly investigated during the past decade, using lipophilic versions of crown-ethers and cryptands as carriers (ref. 1). More recently, lipophilic open-chain tetramines have been tested as carriers for the selective transport of divalent 3d metal ions across membranes (ref. 2). The limit of the type of experiment described above is that, if you have, for instance, an SP layer 1 M in MX_n , at the end of the experiment you will get the RP layer at most 0.5 M in MX_n , leaving 50% of the substrate unextracted. However, 100% M^{n+} extraction can be achieved under three-phase conditions if the transport of the metal ion is coupled to the opposite transport of $n\text{H}^+$ ions. Appropriate systems of formula H_nL , which release $n\text{H}^+$ ions on metal complexation, have been used for the very selective, if not specific, transport of alkaline metals (ref. 3) and of copper(II) ion (ref. 4). In this case, it is said that the metal transport process is *driven by a pH gradient*.

100% transport of ionic species can also be achieved by maintaining a *gradient of redox potential* between the two aqueous phases: this means that one aqueous layer should contain an oxidizing agent (Electron Receiving Phase, ERP) and the other one a reducing agent (Electron Source Phase, ESP). Liquid membrane has to be redox active, i.e. it should contain a lipophilic redox system, whose potential, E_c , is intermediate between that of the aqueous oxidizing agent and that of the aqueous reducing agent ($E_{\text{ox}} > E_c > E_{\text{red}}$). Provided that a salt MX is dissolved in one of the aqueous phases, two possibilities are given: (i) the carrier works through a redox change of the type C/C: M^+ ions and electrons are transported by the reduced form of the carrier ($\text{C}^{\cdot-}, \text{M}^+$) from ESP to ERP, according to the scheme depicted in Figure 1 (ref. 5); (ii) the carrier works through a redox change of the type C^+/C : electrons are transported by the reduced form of the carrier C from ESP to ERP, whereas X^- anions are transported by the oxidized form of the carrier (C^+, X^-) from ERP to ESP (ref. 6). Cross transport of electrons and anions is described in Figure 2.

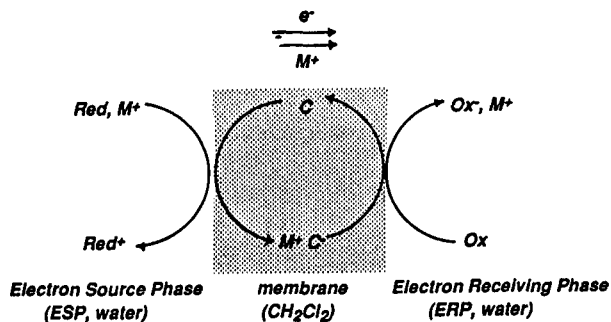


Fig. 1 Parallel transport of electrons and cations across a liquid membrane mediated by a lipophilic C/C^+ redox system.

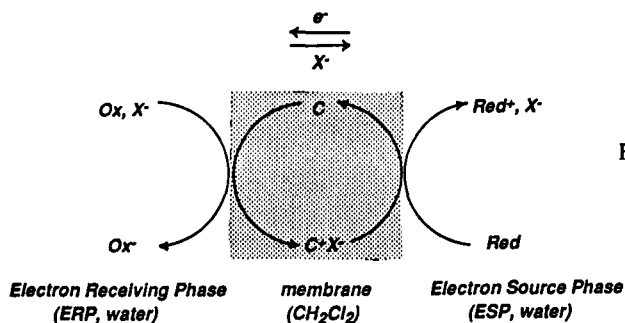
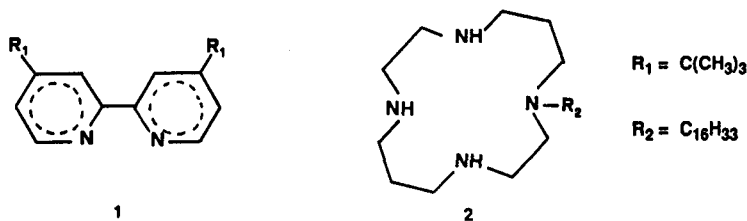


Fig. 2 Cross transport of electrons and anions across a liquid membrane mediated by a lipophilic C^+/C redox system

Transition metal complexes may represent suitable redox systems to be used as electron carriers in that they are usually prone to display one electron reversible redox activity. Moreover, due to the strict dependence of the redox potential upon the stereochemical features of the metal center, structural modifications on the carrier may generate selectivity in the ion/electron transport. An essential requirement to satisfy is that the redox system to be used as an electron carrier possesses such a degree of lipophilicity that it is soluble in the organic phase and insoluble in water. This goal can be easily achieved by appending aliphatic chains on the ligand molecules of the complex which has been chosen for its promising redox properties. In the following, two different types of metal centered redox systems will be considered, whose oxidation and reduction behaviour has been classically investigated through solution chemistry studies: (i) the $[\text{Fe}^{\text{II,III}}(\text{bpy})_3]^{2+,3+}$ system (bpy = 4,4'-di-*tert*-butyl-2,2'-dipyridyl, **1**) and (ii) the $[\text{Ni}^{\text{II,III}}\text{LCl}_2]^{0,+}$ system ($\text{L} = (\text{N-cetyl-cyclam}, \text{2})$). Complex (i) is expected to transfer electrons (in this case, at the membrane/aqueous phase interface) through an *outer sphere* mechanism; system (ii) should exchange electrons through a bridged ligand (*inner sphere*) process.



The aim of this investigation is to assess to what extent the above different features affect rate and selectivity of the ion/electron transport across redox active liquid membranes. Both systems may be referred to the type (ii) (C/C^+) redox behaviour, which originates the anion/electron cross transport described in Fig. 2.

AN OUTER SPHERE ELECTRON CARRIER: $[\text{Fe}^{\text{II,III}}(\text{bpy})_3]^{2+,3+}$

$[\text{Fe}^{\text{II,III}}(2,2'\text{-bipyridyl})_3]^{2+,3+}$ is a classical redox system, which reversibly exchanges one electron according to an *outer sphere* mechanism. However, this system cannot be used as a carrier for the transport of electrons across a bulk CH_2Cl_2 membrane for it partitions between the aqueous and non-aqueous phase. Thus, the more lipophilic ligand 4,4'-di-*tert*-butyl-2,2'-dipyridyl (bpy) was synthesized, whose Fe^{II} and Fe^{III} complexes are not extracted at all in water from the CH_2Cl_2 layer. Voltammetric investigations in a CH_2Cl_2 solution, 0.1 M in Bu_4NClO_4 , allowed to locate the $[\text{Fe}^{\text{III}}(\text{bpy})_3]^{3+}/[\text{Fe}^{\text{II}}(\text{bpy})_3]^{2+}$ redox change at a potential of 0.545 V vs $\text{Fc}^+//\text{Fc}$. Preliminary two-phase experiments indicated that aqueous Ce^{IV} , in HClO_4 solution, is able to oxidize $[\text{Fe}^{\text{II}}(\text{bpy})_3](\text{ClO}_4)_2$ in CH_2Cl_2 to

$[\text{Fe}^{\text{III}}(\text{bpy})_3](\text{ClO}_4)_3$. On the other hand, the CH_2Cl_2 dissolved $[\text{Fe}^{\text{III}}(\text{bpy})_3](\text{ClO}_4)_3$ complex is reduced to the divalent form through equilibration with an aqueous acidic solution of Fe^{II} . Thus, electrochemical scales in water and in CH_2Cl_2 should be juxtaposed in such a way that the potential of the $[\text{Fe}^{\text{III}}(\text{bpy})_3]^{3+}/[\text{Fe}^{\text{II}}(\text{bpy})_3]^{2+}$ redox couple (non-aqueous scale) lies between the potentials of the $\text{Ce}^{\text{IV,III}}$ and $\text{Fe}^{\text{III,II}}$ redox couples (1.70 and 0.77 V vs NHE, respectively, in the aqueous scale). That means that the $[\text{Fe}^{\text{III}}(\text{bpy})_3](\text{ClO}_4)_2$ complex should be able to oxidize, under two-phase conditions, any aqueous reducing agent whose redox potential is lower than 0.77 V vs NHE. As a matter of fact, the green CH_2Cl_2 solution of the Fe^{III} complex turns red (due to reduction to the divalent species) on equilibration with a number of aqueous reducing agents ($[\text{Fe}^{\text{II}}(\text{CN})_6]^{4-}$, NO_2^- , Cr^{2+} , SO_3^{2-}), whose potential values are distinctly lower than 0.77. Subsequently, three-phase (transport) experiments of the type described in Fig. 2 were carried out: in particular, ERP contained Ce^{IV} and HClO_4 , ESP contained one of the previously mentioned reducing agents and was adjusted to 1 M ionic strength by HClO_4 or NaClO_4 , whereas the bulk CH_2Cl_2 membrane was 5×10^{-4} M in $[\text{Fe}^{\text{II}}(\text{bpy})_3](\text{ClO}_4)_2$. Two type of experiments were performed: in a first series, the concentration of Ce^{IV} in ERP was substantially lower than that of the reducing agent in ESP (0.01 and 0.1 M, respectively). In this case, the rate of the cross transport of electrons and ClO_4^- ions, measured through the rate of disappearance of Ce^{IV} in ERP, was the same, independently upon the nature of the employed reducing agent in ESP (Fe^{2+} , NO_2^- , $[\text{Fe}^{\text{II}}(\text{CN})_6]^{4-}$, Cr^{2+}). This may suggest that the *rate determining step* of the transport process takes place at the ERP/membrane interface ($\text{Ce}^{\text{IV}}/[\text{Fe}^{\text{II}}(\text{bpy})_3]^{2+}$ two-phase reaction). On the other hand, if the concentration of the aqueous redox agents in the three-phase experiments is reversed (Ce^{IV} 0.1 M, reducing agent 0.01 M), the rate of the electron transport process, measured through the rate of formation of the oxidized form in ESP, varies according to the nature of the reducing agent, indicating that the *rate determining step* takes place at the membrane/ESP interface ($[\text{Fe}^{\text{III}}(\text{bpy})_3]^{3+}/\text{Red}$ redox process). For instance, for $\text{Red} = [\text{Fe}^{\text{II}}(\text{CN})_6]^{4-}$ the rate of the electron transport is about twice that observed with that observed for $\text{Red} = \text{Fe}^{\text{II}}$. In any case, the rate of the e^-/ClO_4^- cross transport is substantially higher when it is controlled at the ERP/membrane interface, being complete (100% of Ce^{IV} reduced) after 6 hrs. In processes controlled at the other side of the membrane, after 8 hrs only 40% of $[\text{Fe}^{\text{II}}(\text{CN})_6]^{4-}$ has been oxidized (and 20% of Fe^{II}).

AN INNER SPHERE ELECTRON CARRIER: $[\text{Ni}^{\text{II,III}}(\text{N-cetyl-cyclam})\text{Cl}_2]^{0,+}$

When incorporated in the framework of the tetra-aza macrocycle cyclam, metal centres may display unusually rich redox activity. Electron exchange with the redox partner takes place through one of ligands occupying the two axial positions (e.g. Cl^-), according to an inner-sphere mechanism. A well documented example is that of the $\text{Ni}^{\text{II}}/\text{Ni}^{\text{III}}$ redox change. To satisfy the solubility requirements for an electron carrier, a lipophilic version of cyclam was synthesized by appending a C_{16} aliphatic chain at one of the nitrogen atoms of the 14-membered tetramine macrocycle: (*N*-cetyl)-cyclam, in the following indicated by L). $\text{Ni}^{\text{II}}\text{LX}_2$ complexes were synthesized ($\text{X} = \text{Cl}^-$, ClO_4^-), which are soluble in CH_2Cl_2 and insoluble in water. Preliminary two-phase redox experiments indicated that, when dissolved in 1 M NaCl aqueous solution, $\text{Na}_2\text{S}_2\text{O}_8$ oxidizes $[\text{Ni}^{\text{II}}\text{LCl}_2]$ to $[\text{Ni}^{\text{III}}\text{LCl}_2]\text{Cl}$, but, if dissolved in aqueous 1 M NaClO_4 , it does not oxidize $[\text{Ni}^{\text{II}}\text{L}](\text{ClO}_4)_2$. This behaviour, to be referred to the much higher capability of axially bound Cl^- ions to stabilize trivalent nickel, and to lower the $\text{Ni}^{\text{III,II}}$ potential, compared to the less coordinating ClO_4^- ions, opens the way to a *thermodynamic* control, through the simple change of the type of the aqueous background electrolyte, of an electron transport experiment involving the $[\text{Ni}^{\text{II}}\text{LX}_2]/[\text{Ni}^{\text{III}}\text{LX}_2]\text{X}$ redox system as a carrier.

Transport experiments of the type described in Fig. 2 were carried out in which ERP was 0.1 M in $\text{Na}_2\text{S}_2\text{O}_8$ and 1 M in NaCl ($\text{pH} = 7$), the CH_2Cl_2 layer was made 0.001 M in $[\text{Ni}^{\text{II}}\text{LCl}_2]$, and ESP, 1 M in HCl , contained a metal centred reducing agent: Fe^{II} , Ti^{III} , Cr^{II} and $[\text{Co}^{\text{II}}(\text{cage})]$ complex, in 0.01 M concentration ($\text{cage} = 1,9$ -diammonium-3,6,10,13,16,19-hexabicyclo[6.6.6]eicosane). The fact that the concentration of the aqueous oxidizing agent is much greater than that of the aqueous reducing agent may suggest that the *rate determining step* of the transport process takes place at the membrane/ESP interface and is influenced by the nature of the reducing agent employed. Indeed, the rate of the transport of electrons from ESP to ERP (and of chloride ions from ERP to ESP) varies in an outstanding way with the type of the reducing agent. In the experimental conditions described above, times at which the aqueous reducing agent has been completely oxidized ($t_{100\%}$, minutes) are: Ti^{III} : 10; Cr^{II} : 75; Fe^{II} : 450; $[\text{Co}^{\text{II}}(\text{cage})]$: 800.

The sequence of the electron transport rates ($\text{Ti}^{\text{III}} > \text{Cr}^{\text{II}} > \text{Fe}^{\text{II}} > [\text{Co}^{\text{II}}(\text{cage})]$) does not correlate the sequence of the potential of the corresponding couple. The considered reducing metal centres are present in 1 M HCl solution as chloro-complexes or aquo-chloro-complexes and it is possible that the electron transfer process at the membrane/ESP interface involves a species in which a chloride ion bridges the $[\text{Ni}(\text{N-cetyl-cyclam})]$ moiety and the

reducing metal ion. According to this hypothesis, at this stage of the investigation, we cannot explain the substantially different rates of electron transport experiments involving Ti^{III} , Cr^{II} and Fe^{II} . However, it is very reasonable that the $[\text{Co}^{\text{II}}(\text{cage})]$ complex causes the slowest transport since the aliphatic shield of the cage polyamine prevents from the bridging of Co^{II} and Ni^{III} redox centres. Thus, this electron transport experiment is slow since it is controlled by an outer sphere type electron transfer at the membrane/ESP interface.

Direct evaluation of the effect of the *outer* or *inner sphere* mechanism on the overall electron transport rate could be made performing two parallel experiments: (1) $\text{S}_2\text{O}_8^{2-}$ 0.1 M, NaCl 1M/ NiCl_2 0.001 M/ Fe^{II} 0.01 M, HCl 1M; and (2) Ce^{IV} 0.2 M, HClO_4 2.5 M, HNO_3 0.5 M/ $[\text{Fe}^{\text{II}}(\text{bpy})_3](\text{ClO}_4)_3$ 0.001 M/ Fe^{II} 0.01 M, HCl 0.1 M. It has been observed that in experiment (1) 100% reducing agent in ESP was oxidized after 7½ hrs; after the same period of time, in experiment (2), only 20% of Fe^{II} had been oxidized.

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