Ferrocene Derivatives as Electron Carriers for Selective Oxidation and Reduction Reactions through a Liquid Membrane

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1-Hexadecanoyl- and 1-hexadecyl-ferrocene, which undergo one-electron oxidation to the corresponding ferrocenium cations at distinctly different potentials (0.25 and −0.05 V *vs.* ferrocenium–ferrocene, respectively, in dichloromethane solution, 0.1 mol dm^{-3} in NBu_4ClO_4), have been used as carriers for the cross-transport of electrons and perchlorate ions across a bulk dichloromethane membrane. The liquid membrane interfaces an aqueous layer containing $[Fe^{II}(CN)_6]^{4-}$ (the electron source phase, e.s.p) and an aqueous layer containing Ce^{IV} (the electron receiving phase, e.r.p.). The occurrence of the transport is accounted for on the basis of an empirical juxtaposition of the electrochemical scales (*i*) in water and (*ii*) in CH_2Cl_2, which gives the sequence: $E°(Ce^{IV/III}) > E°[Fe(C_5H_5)(C_5H_4COC_{15}H_{31})^{+/0}] > E°[Fe(C_5H_5)(C_5H_4C_{16}H_{33})^{+/0}] > E°[Fe^{III/II}(CN)_6{}^{3-/4-}]$. The special position of the potential of the aqueous Fe^{III}–Fe^{II} couple, which is intermediate between those of the two ferrocene derivatives, makes it possible to carry out selective electron-transport experiments: if the e.r.p. contains a mixture of Ce^{IV} and Fe^{III}, when $[Fe(C_5H_5)(C_5H_4C_{16}H_{33})]$ is used as a carrier, both the oxidizing cations are reduced; when $[Fe(C_5H_5)(C_5H_4COC_{15}H_{31})]$ is used, Ce^{IV} is reduced, but Fe^{III} is left intact. These examples clearly illustrate the novel principle of the selective oxidation and reduction reactions performed under three-phase conditions.

Oxidation and reduction reactions in solution may or may not involve the intimate contact of the reactants and the direct transfer of electrons from the reducing agent (red) to the oxidizing agent (ox). For instance, the solution of red and the solution of ox can be separated by a salt bridge and electrons can flow from red to ox through a metal wire, according to the typical experiment derived from Volta's device. More recently, another procedure has been devised, which keeps the solutions of red and ox separated by a layer of an immiscible liquid. The interfacing liquid layer can be made permeable to electrons by dissolving in it an appropriate molecular redox system C: C should be prone, for instance, to the reversible C–C$^+$ redox change. Thus, the electron transfer from red to ox can take place according to the mechanism illustrated in Fig. 1.

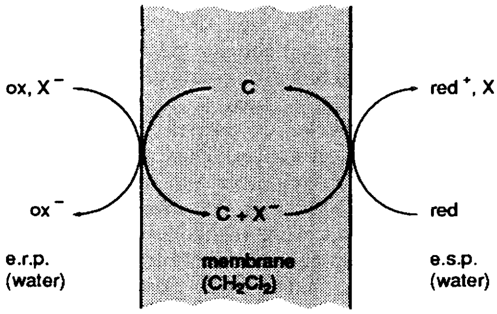
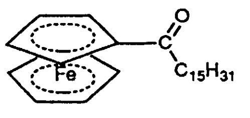


Fig. 1 Cross-transport of electrons and anions across a liquid membrane, mediated by a lipophilic C–C$^+$ redox system

The reduced form C transports electrons from the layer containing red (the electron source phase, e.s.p.) to the layer containing ox (the electron receiving phase, e.r.p.), whereas its oxidized form, C$^+$, transports X$^-$ anions in the opposite direction. If the e.s.p. and e.r.p. are aqueous, the interfacing layer should be a water immiscible liquid (*e.g.* CH_2Cl_2). As the interfacing layer permits selective transport of chemical entities it can be considered as a membrane. The C–C$^+$ redox system works in a cyclic way and needs to be present only in a catalytic amount.

Three-phase oxidation and reduction reactions involving a liquid membrane were first described by Lehn and co-workers,[1] who looked, in particular, at the use of light as a trigger of the electron transport. Subsequent work considered electron carriers of both organic and inorganic nature.[2–4] In particular, we were recently interested in the use of transition-metal complexes as electron carriers and described the e$^-$/X$^-$ cross transport across a bulk CH_2Cl_2 layer by carriers deriving from classical co-ordination chemistry: complexes of synthetic tetraazamacrocycles [*e.g.* 1,4,8,11-tetraazacyclotetradecane (cyclam)][5,6] and tris(2,2′-bipyridine)[7] complexes. The main interest of this type of experiments lies in the possibility of carrying out oxidation and reduction reactions in a selective way. Selectivity derives from the thermodynamic condition on which the experiment described by Fig. 1 is based: the electrode potential associated with the C$^+$–C redox change has to be intermediate between that associated with the ox–ox$^-$ couple and that with the red$^+$–red couple: $E_{ox} > E_C > E_{red}$. This comparison is not straightforward, as the above quantities refer to different media: E_{ox} and E_{red} to the aqueous solution [and are measured *vs.* normal hydrogen electrode (NHE)] and E_C to the membrane solution (to be referred to the half-cell chosen as a standard in that particular medium). If, for instance, two oxidizing agents of distinctly different oxidizing power are present in the e.r.p., it should be possible to reduce one of them and leave intact the other by varying appropriately the value of E_C. The potential of the redox molecular system chosen as an e$^-$/X$^-$ carrier can be modulated by making structural modifications on it (introduction of substituents, steric effects, *etc.*).

To verify this possibility, we chose the most classical organometallic redox agent: ferrocene. The tendency of ferrocene to undergo a fast and reversible one-electron oxidation process to



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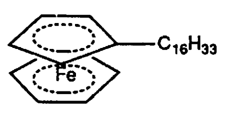

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give the stable ferrocenium ion was demonstrated since its first appearance on the chemical stage.[8] Moreover, this redox couple can be conveniently modulated through the introduction of substituents on the rings.[9] This work describes the design and use of two ferrocene derivatives {1-hexadecanoylferrocene, $[Fe(C_5H_5)(C_5H_4COC_{15}H_{31})]$ **1**; and 1-hexadecylferrocene, $[Fe(C_5H_5)(C_5H_4C_{16}H_{33})]$ **2**} as carriers for the cross transport of electrons (in the reduced ferrocene form) and anions (in the oxidized ferrocenium form) across a dichloromethane liquid membrane, with the aim of carrying out selective oxidation and reduction reactions using aqueous solutions containing a mixture of conventional redox agents.

Experimental

Materials.—1-Hexadecanoylferrocene **1** was obtained through the $AlCl_3$-catalysed acylation of ferrocene, 1-hexadecylferrocene **2** by Clemmensen reduction of **1**.[10]

Electrochemistry.—The $E_{\frac{1}{2}}$ values pertinent to the $[Fe(C_5H_5)(C_5H_4R)]$–$[Fe(C_5H_5)(C_5H_4R)]^+$ redox change were determined by cyclic voltammetry in a dichloromethane solution, which was made 0.1 mol dm^{-3} in NBu_4ClO_4 (Fluka, purissimum). A glass cell, thermostatted at 25 °C by circulating water, was used, equipped with three electrodes: a platinum microsphere (the working electrode), a platinum foil (the counter-electrode) and a silver wire (the pseudo-reference electrode, to be calibrated with an internal standard). Potentials in this work are reported *vs.* the ferrocenium–ferrocene $[Fe(C_5H_5)_2]^+$–$[Fe(C_5H_5)_2]$ couple, which is the most widely accepted reference system for non-aqueous solutions.[11] However, ferrocene could not be used as internal standard, as its oxidation wave superimposes partially with those of the investigated ferrocene derivatives. Thus, tris(4,4′-di-*tert*-butyl-2,2′-bipyridine)iron(II) perchlorate was used as an internal standard [$E_{\frac{1}{2}}(Fe^{III,II})$ = 550 V *vs.* ferrocenium–ferrocene][7] and the measured potentials were then referred to ferrocenium–ferrocene. Cyclic voltammetry profiles were obtained by a PAR model 273 potentiostat/galvanostat, driven by an IBM AT personal computer, through dedicated software.

Electron Transport Experiments.—Transport experiments were carried out in a V-shaped glass cell, the design of which has been described.[5] In a typical experiment, the cell was charged with a dichloromethane solution (30 cm^3) of the ferrocene derivative used as a carrier. In each arm of the cell, an aqueous layer (30 cm^3) containing the redox agent of interest was carefully stratified over the dichloromethane layer. The membrane was magnetically stirred, at a controlled rate (200 ± 10 revolutions min^{-1}). The aqueous layers were stirred mechanically by two T-shaped Teflon stirring rods of equal surface area and driven by twin electrical motors, at a rate adjusted by a potentiometer and calibrated by a stroboscope: 200 ± 10 revolutions min^{-1} was chosen. Solutions were transferred to the cell under dinitrogen and dinitrogen saturated in CH_2Cl_2 flowed in both arms of the cell during the transport experiments. Experiments were carried out in a room thermostatted at 25 ± 1 °C.

The progress of the electron transport was followed by monitoring the concentration of the chosen redox agent. A 5 μl volume of the solution was extracted by a syringe at selected time intervals and transferred under dinitrogen to a 1 mm quartz cuvette. The concentration of the species of interest was evaluated through the intensity of a typical absorption band: Ce^{IV} (310 nm), $[Fe^{III}(CN)_6]^{3-}$ (420 nm). In the case of Fe^{III}, in an experiment in which the e.r.p. contained only Fe^{III}, a measured volume of concentrated hydrochloric acid was added to the extracted portion to make the iron(III) absorption band conveniently intense (360 nm, pertinent to the $FeCl_4^-$ species). When Ce^{IV} was also present in the e.r.p., a solution of 2 mol dm^{-3} NH_4SCN was added to the extracted portion and Fe^{III} was determined through the band at 480 nm, pertinent to the $[Fe^{III}(SCN)_6]^{3-}$ chromophore. The determination of the ClO_4^- ion in the e.s.p. was carried by extraction of the anion into a butyronitrile layer from a portion of the aqueous phase, to which $[Fe^{II}(phen)_3]SO_4$ (phen = 1,10-phenanthroline) had been added, as described.[11] The concentration of ClO_4^- was obtained from the intensity of the absorption band at 510 nm. Spectra were measured on a Cary 2300 (Varian) UV/VIS/NIR spectrophotometer.

Results and Discussion

Designing the Carrier C *and modulating the* C–C$^+$ *Redox Couple Potential.*—An essential requirement a redox system has to satisfy in order to be used as an electron carrier is that both the reduced and oxidized forms, C and C$^+$, are fairly soluble in the solvent used as a liquid membrane and completely insoluble in water. In this connection, ferrocene is soluble in CH_2Cl_2, the solvent to be used as a liquid membrane. Moreover, if a layer of CH_2Cl_2 containing ferrocene is equilibrated with an aqueous layer, the ferrocene does not partition between the two immiscible liquids and remains confined in the non-aqueous phase. However, if such a layer (*e.g.* 10^{-3} mol dm^{-3}) is treated with an equal volume of an aqueous solution 10^{-2} mol dm^{-3} in Ce^{IV} and 1 mol dm^{-3} in $HClO_4$, ferrocene to ferrocenium oxidation takes place under two-phase conditions. Yet, ferrocenium goes into the aqueous phase, as shown by the appearance, in the spectrum of the aqueous layer, of the absorption band centred at 628 nm, typical of the ferrocenium ion. Thus, plain ferrocene cannot be used as an electron carrier and, to do the job conveniently, the ferrocene framework has to be made definitively lipophilic. This has been done by appending on one of its rings a long carbon chain, in particular a C_{16} chain. Two C_{16} ferrocene derivatives have been chosen: 1-hexadecanoylferrocene **1**, which can be obtained through the Friedel-Craft acylation of ferrocene, and 1-hexadecylferrocene **2**, obtained through the Clemmensen reduction of **1**. Both derivatives exhibit the required properties of an electron carrier: (*i*) uncomplicated and reversible one-electron redox activity and (*ii*) complete hydrophobicity of the reduced and oxidized forms.

The redox behaviour of the two derivatives was first characterized through cyclic voltammetry studies on dichloromethane solutions, made 0.1 mol dm^{-3} in NBu_4ClO_4, at 25 °C. Both compounds display reversible one-electron behaviour at the working platinum electrode. However, the $E_{\frac{1}{2}}$ values are rather different: oxidation of compound **1** takes place at a potential 0.25 V more positive than observed for plain ferrocene, under the same conditions. The more positive value of $E_{\frac{1}{2}}$, *i.e.* the more difficult oxidation of **1** compared to ferrocene, reflects the electron-withdrawing effect exerted by the RCO substituent. On the other hand, oxidation of **2** takes place at a potential of -0.05 V; the moderately negative value is to be ascribed to the 'electron pumping' effect exerted by the appended aliphatic chain. In any case, the difference between the $E_{\frac{1}{2}}$ values of the two ferrocene derivatives, *ca.* 300 mV, seems large enough to envisage selectivity effects in oxidation and reduction processes under two- and three-phase conditions.

Redox Processes at the Dichloromethane–Water Interface.—A dichloromethane solution 10^{-3} mol dm^{-3} in compound **1** or **2**, of typical yellow-orange colour, if equilibrated (*i.e.* vigorously shaken for a few seconds) with an equal volume of an aqueous solution 10^{-2} mol dm^{-3} in Ce^{IV} and 1 mol dm^{-3} in $HClO_4$ turns

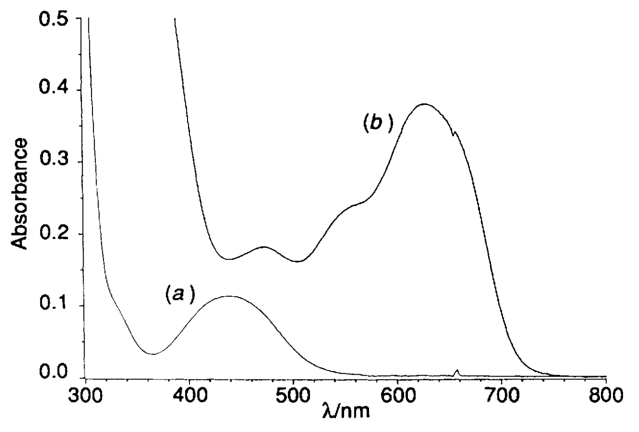

Fig. 2 Absorption spectra of CH_2Cl_2 solutions 10^{-3} mol dm^{-3} in (*a*) compound **2**, (*b*) $[Fe(C_5H_5)(C_5H_4C_{16}H_{33})]ClO_4$. Solution (*b*) was obtained by equilibrating solution (*a*) with an aqueous layer containing Ce^{IV} and $HClO_4$

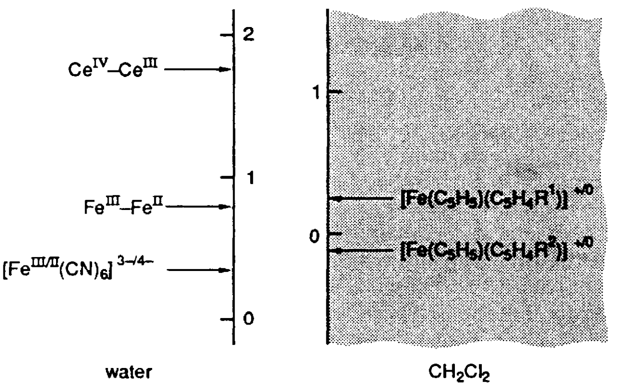

Fig. 3 Tentative juxtaposition of the electrochemical scales in water (left hand) and in dichloromethane solution (right hand). This juxtaposition is merely empirical and derives from two-phase oxidation and reduction experiments. $R^1 = OCC_{15}H_{31}$, $R^2 = C_{16}H_{33}$

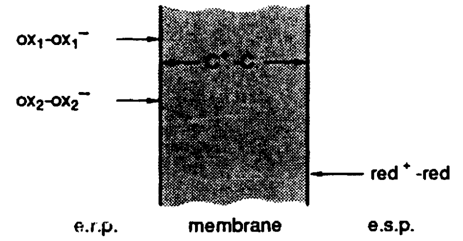

Fig. 4 Pictorial representation of the principle of selective oxidation and reduction under three-phase conditions. The aqueous reducing agent red, profiting from the filtering effect exerted by the membrane-dissolved C–C$^+$ redox system, will reduce ox 1, but will leave ox 2 intact. Note that under homogeneous conditions (*e.g.* in aqueous solution) red would reduce both ox 1 and ox 2

blue-green. The colour change of the dichloromethane layer is related to the two-phase redox process (1). These findings

$$[Fe(C_5H_5)(C_5H_4R)](CH_2Cl_2) + Ce^{IV}(aq) + ClO_4^-(aq) \rightleftharpoons [Fe(C_5H_5)(C_5H_4R)^+,ClO_4^-](CH_2Cl_2) + Ce^{III}(aq) \quad (1)$$

indicate that aqueous Ce^{IV}, in 1 mol dm^{-3} $HClO_4$ ($E° = 1.70$ V *vs.* NHE),[12] is a stronger oxidizing agent than the $[Fe(C_5H_5)(C_5H_4R)^+,ClO_4^-]$ ion pair, in dichloromethane solution. This would suggest that the two electrochemical scales in water and in CH_2Cl_2 should be juxtaposed in such a way that the potential associated with the aqueous Ce^{IV}–Ce^{III} couple is higher than those associated with the $[Fe(C_5H_5)(C_5H_4R)]^+$–$[Fe(C_5H_5)(C_5H_4R)]$ couples in the CH_2Cl_2 solution ($R = OCC_{15}H_{31}$ or $C_{16}H_{33}$).

The oxidized species $[Fe(C_5H_5)(C_5H_4R)^+,ClO_4^-]$ can be quantitatively reduced to the original ferrocene form by treatment, under two-phase conditions, with a mild aqueous reducing agent such as $[Fe^{II}(CN)_6]^{4-}$ ($E° = 0.36$ V *vs.* NHE), as shown by the orange colour of the dichloromethane layer (and complete disappearance of the ferrocenium band at 628 nm). The two-phase redox process is described by equation (2).

$$[Fe(C_5H_5)(C_5H_4R)^+,ClO_4^-](CH_2Cl_2) + [Fe^{II}(CN)_6]^{4-}(aq) \rightleftharpoons [Fe(C_5H_5)(C_5H_4R)](CH_2Cl_2) + [Fe^{III}(CN)_6]^{3-}(aq) + ClO_4^-(aq) \quad (2)$$

Fig. 2 displays the spectra of the reduced and oxidized forms for $R = C_{16}H_{33}$.

The above findings allowed us better to adjust the relative positions of the electrochemical scales in water and in CH_2Cl_2. In particular, the two scales should be juxtaposed in such a way that the potentials pertinent to the $[Fe(C_5H_5)(C_5H_4R)]^+$–$[Fe(C_5H_5)(C_5H_4R)]$ couples are higher than that associated with the aqueous $[Fe^{III}(CN)_6]^{3-}$–$[Fe^{II}(CN)_6]^{4-}$ couple and lower than that associated with the aqueous Ce^{IV}–Ce^{III} couple.

Selectivity effects induced by the R substituent are observed with two-phase experiments involving the aqueous Fe^{III}–Fe^{II} couple: 10^{-2} mol dm^{-3} Fe^{III} in 1 mol dm^{-3} $HClO_4$ oxidizes compound **2**, under two-phase conditions, but not **1**. On the other hand, 10^{-2} mol dm^{-3} Fe^{II} in 1 mol dm^{-3} $HClO_4$ reduces, under two-phase conditions, $[Fe(C_5H_5)(C_5H_4COC_{15}H_{31})]^+$ but not $[Fe(C_5H_5)(C_5H_4C_{16}H_{33})]^+$, as demonstrated by the appropriate colour changes and by spectral characterization. All the above evidence indicates that the two electrochemical scales in water and CH_2Cl_2 should be juxtaposed as shown in Fig. 3. In particular, the potential associated with the aqueous Fe^{III}–Fe^{II} couple (0.77 V *vs.* NHE) should be less positive than that of the $[Fe(C_5H_5)(C_5H_4R)]^+$–$[Fe(C_5H_5)(C_5H_4R)]$ when $R = OCC_{15}H_{31}$ but more positive when $R = C_{16}H_{33}$, in CH_2Cl_2. Such a situation opens the route to experiments of selective electron transport across liquid membranes.

Liquid Membranes as Electron Filters.—Moving the redox potential E_C, associated with the redox system used as a carrier, up and down along the electrochemical scale may allow one to perform oxidation and reduction processes in a selective way, as illustrated in Fig. 4. For instance, let the e.r.p. contain two oxidizing agents ox 1 and ox 2 exhibiting distinctly different reduction potentials (in particular: $E_{ox1} > E_{ox2}$). The e.s.p. contains a reducing agent red, the potential of which is low enough to reduce both ox 1 and ox 2. This double reduction will obviously take place simultaneously under single-phase conditions, in the absence of exotic kinetic effects, if a solution containing equivalent or excess of red is poured into a solution containing ox 1 and ox 2. Moreover, the *simultaneous* reduction of ox 1 and of ox 2 will take place also under three-phase conditions, provided the membrane contains a redox system C, whose potential E_C is lower than E_{ox2} (and higher than E_{red}). On the other hand, *selective* reduction of ox 1 in presence of ox 2 will take place if E_C has an intermediate value between E_{ox1} and E_{ox2}. This situation is illustrated in Fig. 4. In these circumstances, ox 1 will be reduced, whereas ox 2 will be left intact. In this sense the carrier-containing membrane behaves as a filter for electrons. The permeability of the filter can be regulated by modulating the potential associated with the C^+–C redox change. For a given type of carrier, the potential can be modulated through subtle synthetic modifications (*e.g.* by changing the nature of the substituents). Compounds **1** and **2** possess the required properties and have been used as carriers in electron-transport experiments to test the principle of selective

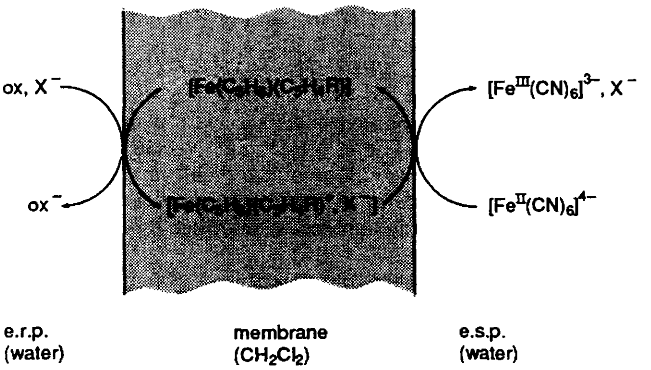

Fig. 5 Cross-transport of electrons and anions ($X^- = ClO_4^-$) across a dichloromethane membrane, mediated by an $[Fe(C_5H_5)(C_5H_4R)]^{0/+}$ redox system. For R = $C_{16}H_{33}$, the transport proceeds if ox is either Ce^{IV} and Fe^{III}; for R = $C_{15}H_{31}CO$, it proceeds if ox is Ce^{IV} but not Fe^{III}

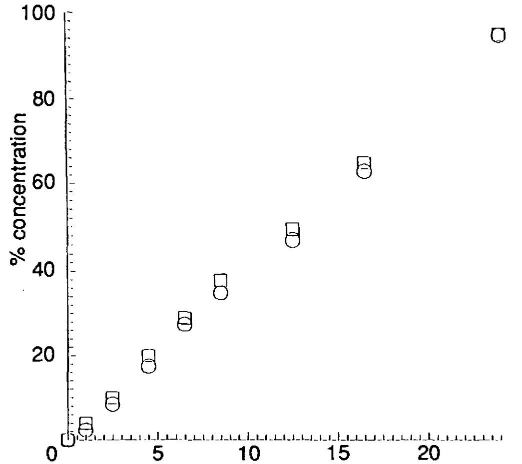

Fig. 6 Time-dependent concentration profiles (in %) for $[Fe^{III}(CN)_6]^{3-}$ (○) and ClO_4^- (□) in the e.s.p. Superimposition of the two profiles demonstrates the 1:1 stoichiometry of the e^-/ClO_4 cross-transport

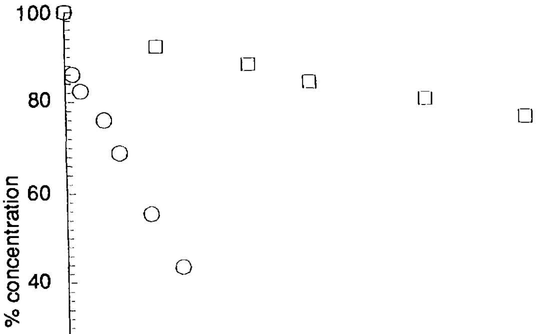

Fig. 7 Electron-transport experiments mediated by the membrane-dissolved $[Fe(C_5H_5)(C_5H_4C_{16}H_{33})]^{0/+}$ redox system. The e.s.p. contained $[Fe^{II}(CN)_6]^{4-}$, e.r.p. Ce^{IV} or Fe^{III}. The time-dependent concentration (%) profiles of Ce^{IV} (○) and Fe^{III} are shown. Under the same experimental conditions, Ce^{IV} is reduced much faster than is Fe^{III}

oxidation and reduction reactions under three-phase conditions.

Ferrocene Derivatives as Carriers of Electrons and of Perchlorate Ions.—Prior to describing selective oxidation and reduction reactions by using liquid membranes, it is necessary to characterize the mechanism of the cross-transport of electrons and anions, driven by a gradient of redox potential and mediated by the $[Fe(C_5H_5)(C_5H_4R)]$–$[Fe(C_5H_5)(C_5H_4R)]^+$ system. In a typical experiment, the V-shaped glass cell was charged with a dichloromethane solution (30 cm^3) 10^{-3} mol dm^{-3} in the carrier, *e.g.* **2** (the liquid membrane). The dichloromethane layer separated the e.s.p. {30 cm^3 of an aqueous solution 0.01 mol dm^{-3} in $[Fe^{II}(CN)_6]^{4-}$} and the e.r.p. (30 cm^3 of an aqueous solution 0.05 mol dm^{-3} in Ce^{IV} and 1 mol dm^{-3} in $HClO_4$). The occurrence and progress of the electron transport was demonstrated by the appearance and the gradual increase in the concentration of $[Fe^{III}(CN)_6]^{3-}$ in the e.s.p., as monitored through the ferricyanide band at 420 nm. The mechanism of transport is illustrated in Fig. 5.

Electrons are transported across the membrane by the reduced form of the carrier, *e.g.* $[Fe(C_5H_5)(C_5H_4R)]$, from aqueous $[Fe^{II}(CN)_6]^{4-}$ to aqueous Ce^{IV}. The mechanism outlined implies that, to maintain electroneutrality, ClO_4^- ions are transported from the e.r.p. to the e.s.p. by the carrier in its oxidized form, $[Fe(C_5H_5)(C_5H_4R)]^+$. Thus, the e.s.p. solution was analysed at selected time intervals for the perchlorate ion. After 1 h the concentration of ClO_4^- was high enough to be detected and analytically determined. Fig. 6 reports the time-dependent variation of the perchlorate concentration. Noticeably, this plot superimposes well, within the experimental error, with the increase in $[Fe^{III}(CN)_6]^{3-}$ concentration. Fig. 6 unequivocally demonstrates the simultaneous occurrence of the cross-transport of electrons and perchlorate anions and clearly defines its 1:1 stoichiometry. It should be noted that, after a few minutes, the originally orange liquid membrane takes a blue colour, due to the formation of $[Fe(C_5H_5)(C_5H_4R)]^+$. This indicates that the two-phase oxidation of $[Fe(C_5H_5)(C_5H_4R)]$, taking place at the e.r.p.–membrane interface, is faster than the reduction of $[Fe(C_5H_5)(C_5H_4R)]^+$, which occurs, under two-phase conditions, at the other side of the membrane. This makes the ferrocenium ion accumulate in the dichloromethane layer, which becomes blue. The higher rate of the two-phase oxidation can be ascribed to the fact that the aqueous oxidizing agent (Ce^{IV}) is present in a much higher concentration than is the aqueous reducing agent $[Fe^{II}(CN)_6]^{4-}$.

Electron Transport Experiments using Compound **1** *or* **2** *as a Carrier.*—Further three-phase experiments were made in order to compare the transport properties of the two envisaged carriers, **1** or **2**. The liquid membrane (30 cm^3) was 0.001 mol dm^{-3} in **1** or **2** and separated an e.s.p. layer (30 cm^3), which was 0.10 mol dm^{-3} in $[Fe^{II}(CN)_6]^{4-}$ and had been adjusted to 1 mol dm^{-3} ionic strength with $NaClO_4$, and an e.r.p. layer (30 cm^3), which was 0.01 mol dm^{-3} in Ce^{IV} or in Fe^{III} and 1 mol dm^{-3} in $HClO_4$. In this case, attention was totally centred on the electron transport and, to exclude the influence of any gradient other than that of the redox potential, the concentration of ClO_4^- had been adjusted at the same value (1 mol dm^{-3}) in both e.s.p. and e.r.p. Moreover, in the present experiment, the limiting reagent was the oxidizing agent, Ce^{IV} or Fe^{III}, which was present in a substantially lower concentration (10 times) than that of the reducing agent $[Fe^{II}(CN)_6]^{4-}$. Let us first consider the experiments in which **2** was used as a carrier. In the two types of experiment (ox = Ce^{IV} or Fe^{III}) it was observed that the rate-determining step of the overall three-phase redox process took place at the e.r.p.–membrane interface. The liquid membrane maintained the orange colour of the reduced form of the carrier, **2**, *i.e.* the two-phase reduction of $[Fe(C_5H_5)(C_5H_4C_{16}H_{33})]^+$ was substantially faster than the two-phase oxidation of **2**. The occurrence of electron transport was demonstrated by the decrease in concentration of the aqueous oxidizing agent Ce^{IV} (or Fe^{III}) in the e.r.p., monitored spectrophotometrically. The variation with time of the amount of the oxidizing agent in the e.r.p. for the two experiments is shown in Fig. 7.

Fig. 7 shows that the three-phase process is much faster when

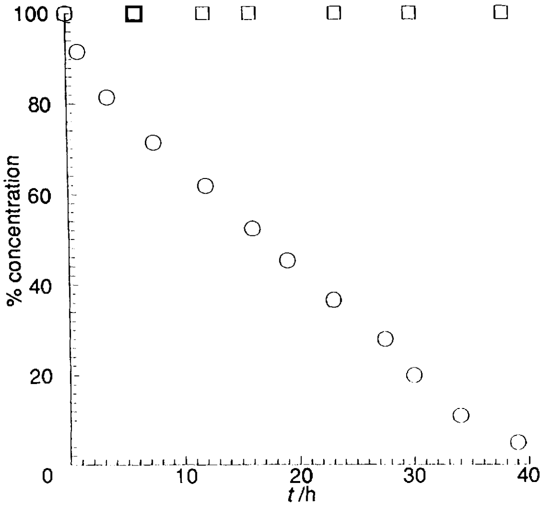

Fig. 8 Electron-transport experiments mediated by the membrane-dissolved $[Fe(C_5H_5)(C_5H_4COC_{15}H_{31})]^{0/+}$ redox system. The e.s.p. contained $[Fe^{II}(CN)_6]^{4-}$, e.r.p. Ce^{IV} or Fe^{III}. Profiles as in Fig. 7. Under the same experimental conditions, Ce^{IV} is reduced, Fe^{III} is not

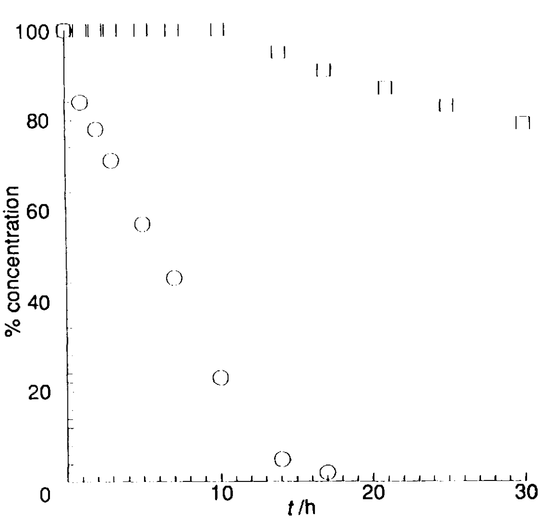

Fig. 9 Electron-transport experiments mediated by the membrane-dissolved $[Fe(C_5H_5)(C_5H_4C_{16}H_{33})]^{0/+}$ redox system. The e.s.p. contained $[Fe^{II}(CN)_6]^{4-}$, the e.r.p. both Ce^{IV} and Fe^{III}. Profiles as in Fig. 7. Ce^{IV} and Fe^{III} are consecutively reduced

ox = Ce^{IV} than when ox = Fe^{III}. This kinetic effect probably derives from the different rates of the electron-transfer processes from the reduced carrier to the aqueous oxidizing agent, which take place somewhere in the borderline region between the membrane and the e.r.p. At this stage of the investigation, nothing is known about the nature and the mechanism of these processes. However, it is reasonable to assume that the crucial step involves the intimate contact of the two reagents and that the electron is transferred through an outer-sphere mode (imposed by the nature of the ferrocene carrier). In this situation, a Marcus-type equation should hold.[13] Thus, the rate constant of the two-phase redox process should increase (*i*) with increasing ΔE $\{=E_{ox} - E[Fe(C_5H_5)(C_5H_4R)]\}$ and (*ii*) with the self-exchange constant k_{11} pertinent to the aqueous oxidizing agent. Whereas the self-exchange constants are similar [k_{11} = 4.4 (Ce^{IV}), 4.0 (Fe^{III})],[14] the remarkably higher value of E_{ox} should favour significantly the rate of the process involving Ce^{IV}, compared to Fe^{III}.

Then, three-phase experiments, under the same experimental conditions as above, were carried out by using compound **1** as an electron carrier. When ox = Ce^{IV} the electron-transport process occurs, as indicated by a progressive decrease in the concentration of Ce^{IV} in the e.r.p., illustrated in Fig. 8. It should be noted that the slope of the transport profile (the concentration of Ce^{IV} *vs.* time) is lower than that observed for the corresponding experiment in which compound **2** was used as a carrier, indicating a distinctly slower electron transfer process at the membrane–e.r.p. interface. This effect could be again interpreted in terms of a Marcus-type equation, considering that, owing to the more positive value of the $[Fe(C_5H_5)(C_5H_4COC_{15}H_{31})]^+$–$[Fe(C_5H_5)(C_5H_4COC_{15}H_{31})]$ redox potential, the ΔE $\{=E_{Ce^{IV}} - E[Fe(C_5H_5)(C_5H_4R)]\}$ term should be smaller than that observed for the process involving the couple $[Fe(C_5H_5)(C_5H_4C_{16}H_{33})]^+$–$[Fe(C_5H_5)(C_5H_4C_{16}H_{33})]$. When ox = Fe^{III} no variation in the concentration of the aqueous oxidizing agent was observed (see Fig. 8), indicating that the electron-transport process does not take place. In particular, no electron transfer takes place from **1** to the aqueous Fe^{III} at the membrane–e.r.p. interface. This behaviour is expected on the basis of the two-phase experiments described before and of the hypothesized juxtaposition of the electrochemical scales in water and in CH_2Cl_2, as shown in Fig. 3. Compound **1** is a rather poor reducing agent and Fe^{III} is too mild a oxidizing agent to oxidize it. An especially strong oxidizing agent such as Ce^{IV} is required to take electrons from **1** and to promote the three-phase redox process.

Selective Reduction of Ce^{IV} *in the Presence of* Fe^{III} *using* $[Fe^{II}(CN)_6]^{4-}$.—Cerium(IV) [$E°(Ce^{IV}$–$Ce^{III}) = 1.77$ V *vs.* NHE] and Fe^{III} [$E°(Fe^{III}$–$Fe^{II}) = 0.77$ *vs.* NHE] are simultaneously reduced by $[Fe^{II}(CN)_6]^{4-}$ ($E°\{[Fe^{III}(CN)_6]^{3-}$–$[Fe^{II}(CN)_6]^{4-}\} = 0.36$ V *vs.* NHE) under single-phase conditions. The two- and three-phase experiments described in the preceding paragraphs suggest that the use of a redox-active liquid membrane containing either compound **1** or **2** as electron carrier may allow simultaneous or selective reduction, respectively. In order to verify this possibility, experiments were made in which the e.r.p. contained both Ce^{IV} and Fe^{III}. In a first experiment, the liquid membrane (30 cm^3) was 0.001 mol dm^{-3} in **2** and separated an e.s.p. layer (30 cm^3), which was 0.10 mol dm^{-3} in $[Fe^{II}(CN)_6]^{4-}$ and had been adjusted to 1 mol dm^{-3} ionic strength with $NaClO_4$, and an e.r.p. layer (30 cm^3), which was 0.01 mol dm^{-3} in Ce^{IV} and 0.01 mol dm^{-3} in Fe^{III} and 1 mol dm^{-3} in $HClO_4$. The occurrence of electron transport was demonstrated by the decrease in concentration of Ce^{IV} in the e.r.p., monitored spectrophotometrically, as shown in Fig. 9. This curve superimposes well, within experimental error, with that observed in the experiment in which only Ce^{IV} was present in the e.r.p., as an oxidizing agent. On the contrary, the concentration profile of Fe^{III} remains at 100% in the first part of the diagram, in particular until the concentration of Ce^{IV} has reached 5% or less. At this time the concentration of Fe^{III} begins to decrease, with a slope comparable to that observed in the experiment in which only Fe^{III} was present in the e.r.p. It is possible that reduction of Fe^{III} at the e.r.p.–membrane interface takes place from the beginning of the experiment, simultaneously with the reduction of Ce^{IV}, even if at a lower rate. However, the Fe^{II} that forms should be immediately reoxidized by the Ce^{IV} present in the aqueous layer. Iron(II) persists in the e.r.p. and can be analytically detected only when all the Ce^{IV} has been reduced.

In the second experiment the conditions described above were maintained, but the membrane contained compound **1**. Again, the concentrations of Ce^{IV} and Fe^{III} were monitored spectrophotometrically and their variation with the time is shown in Fig. 10. The concentration of Ce^{IV} decreases according to a profile which superimposes well with that observed for the experiment in which only Ce^{IV} was present in the e.r.p. (see Fig. 8). The Fe^{III} stays intact and its concentration remains at 100%, even when the Ce^{IV} has been completely reduced. Thus, the three-phase redox process is selective. The term selective deserves a comment: in particular, selectivity does not strictly refer to the process taking place at the membrane–e.r.p. interface. Here, **1** reduces Ce^{IV} under two-phase conditions, but

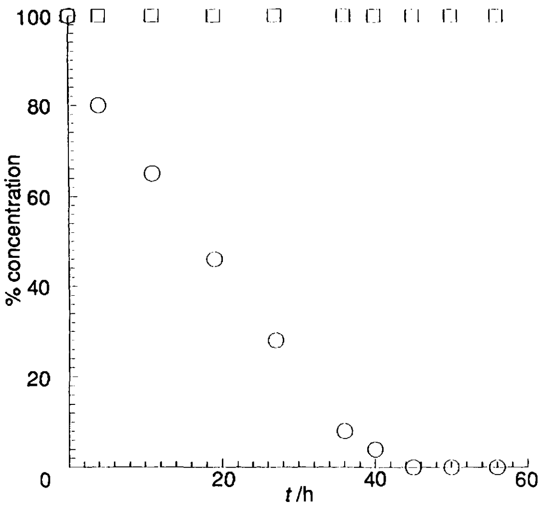

Fig. 10 Electron-transport experiments mediated by the membrane-dissolved $[Fe(C_5H_5)(C_5H_4C_{16}H_{33})]^{0/+}$ redox system. The e.s.p. contained $[Fe^{II}(CN)_6]^{4-}$, the e.r.p. both Ce^{IV} and Fe^{III}. Profiles as in Fig. 7. Ce^{IV} is selectively reduced in the presence of Fe^{III}, the Fe^{III} remains intact even when all the Ce^{IV} has been completely reduced

not Fe^{III}, because the latter has too low a reduction potential. Therefore, the two-phase process is not selective, but it is simply controlled by the electrochemical scale. Rather, attention should be drawn to the aqueous reducing agent $[Fe^{II}(CN)_6]^{4-}$. Under homogeneous conditions, $[Fe^{II}(CN)_6]^{4-}$ would behave as a non-selective reducing agent and would simultaneously reduce both Ce^{IV} and Fe^{III}, present in the same solution. On the other hand, when the redox-active liquid membrane is used, $[Fe^{II}(CN)_6]^{4-}$ is able to 'choose' Ce^{IV} in the presence of Fe^{III}, due to the mediation of the membrane-dissolved carrier **1**.

Conclusion

This work has demonstrated that, using devices based on a redox-active liquid membrane, it is possible to carry out oxidation and reduction reactions in a selective way. Selectivity is not provided by the other known device that allows redox reactions to take place while keeping the solutions of the reagents separated: the voltaic electrical cell. For instance, in a voltaic cell in which one half-cell contains $[Fe^{II}(CN)_6]^{4-}$ and the other one Ce^{IV} and Fe^{III}, both the oxidizing cations will be indirectly reduced by ferrocyanide, according to a time sequence which follows the order of the reduction potentials: Ce^{IV} first, then Fe^{III}. On the contrary, the liquid membrane behaves as a filter, whose permeability to electrons can be regulated by choosing as a carrier a redox system of the appropriate potential. In particular, a membrane containing compound **1** 'filters' only electrons to Ce^{IV}, whereas Fe^{III} is left indefinitely intact in the solution.

Redox-active liquid membranes may become useful tools in separation science and technology. They could be used, for instance, in the pretreatment of a mixture of metal ions, in order to convert some wanted cation, by oxidation or reduction, into an oxidation state more favourable to selective extraction (to be carried out by a membrane procedure, too). Synthetic applications can also be envisaged, in particular when it is important to avoid contamination of the desired product by the other reagent and when the oxidizing or reducing power of a redox agent has to be modulated. In any case, for application purposes, more sophisticated and efficient devices than that employed in this investigation should be used: impregnated hollow fibres appear today as the most promising and versatile version of supported liquid membranes and their use has been recommended.[15,16] However, bulk liquid membrane devices of the type used in this work remain convenient tools to test novel carrier systems and to design transport experiments in the laboratory.

Acknowledgements

This work has been supported by the Italian National Council of Research (CNR, Rome), Progretto Finalizzato Chimica Fine II.

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Received 19*th November* 1991; *Paper* 1/05880K