Metal Complexes that transport Electrons across Liquid Membranes: the $[Fe^{II,III}L_3]^{2+,3+}$ Redox System (L = 4,4′-di-*tert*-butyl-2,2′-bipyridine)

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The lipophilic complex $[Fe^{II}L_3][ClO_4]_2$ (L = 4,4′-di-*tert*-butyl-2,2′-bipyridine) has been prepared to be used as a carrier for the transport of electrons from an aqueous oxidizing phase to an aqueous reducing phase, separated by a CH_2Cl_2 bulk liquid membrane. Two-phase redox experiments indicated that the CH_2Cl_2-dissolved $[Fe^{II}L_3][ClO_4]_2$ complex is oxidized by aqueous Ce^{IV} to give $[Fe^{III}L_3][ClO_4]_3$. On the other hand, $[Fe^{III}L_3][ClO_4]_3$ can be reduced, under two-phase conditions, by a series of aqueous reducing agents according to the rate sequence: $NO_2^- > [Fe^{II}(CN)_6]^{4-} > Fe^{II} > SO_3^{2-}$. Three-phase experiments have been carried out in which electrons are transported by $[Fe^{II}L_3][ClO_4]_2$ from the aqueous reducing phase to the aqueous phase containing Ce^{IV}, across the bulk liquid membrane, and ClO_4^- ions are transported by $[Fe^{III}L_3][ClO_4]_3$ in the opposite direction. The rate of the electron transport is controlled by the rate of the slowest of the two redox processes at the two sides of the membrane. By varying the concentrations of the aqueous reactants, it is possible to determine the two-phase rate-determining step of the overall three-phase process and to perform selective oxidation by Ce^{IV} of the investigated reducing agents.

The most classical of chemical reactions in solution, the oxidation and reduction reaction, can be carried out in two distinct ways: (*i*) by adding a solution of one of the reactants to a solution of the other reactant, causing direct and intimate transfer of electrons from the reducing agent to the oxidizing agent; (*ii*) by connecting the separate solutions of the two reactants through a salt bridge and making electrons flow through a metallic support (electrodes and wire) from the reducing solution to the oxidizing solution (to give a voltaic cell). Reactions of type (*ii*) can be considered as three-phase processes (solution–metal–solution), and, even if more recent than single-phase redox processes, they have been known to the scientific community for a couple of centuries, *i.e.* since the experiments made by Alessandro Volta[1] in 1800, at the University of Pavia.

A novel method has been devised that permits oxidation and reduction processes to be performed under three-phase conditions, keeping the solutions of the two reactants separated. Separation is achieved by interfacing the aqueous reducing solution and the aqueous oxidizing solution by a layer of a water-immiscible liquid (*e.g.* CH_2Cl_2).[2–7] The three-phase system works, *i.e.* the redox reaction takes place, if the non-aqueous layer (to be defined liquid membrane) contains a redox-active molecular system capable of taking up electrons from the aqueous reducing agent (red) at the membrane–aqueous reducing phase interface and, after it has diffused across the membrane to the membrane–aqueous oxidizing phase interface, of releasing electrons to the aqueous oxidizing agent (ox). The lipophilic redox system has to be present not in equimolar amounts to the red and ox reactants, but at a much lower concentration level, for it can travel back and forth across the liquid membrane carrying electrons (and ions) until the limiting aqueous redox reagent has been exhausted. A condition for electron transport is that the potential associated with the redox change of the membrane-dissolved system, E_c, is lower than that associated with the ox–ox$^-$ redox couple, but higher than that associated with the red$^+$–red redox couple ($E_{ox} > E_c > E_{red}$). Moreover, in order to maintain electroneutrality in the membrane, ions must flow across the membrane simultaneously with electrons. The type of charge of the flowing ions depends upon the type of redox change which takes place inside the membrane.

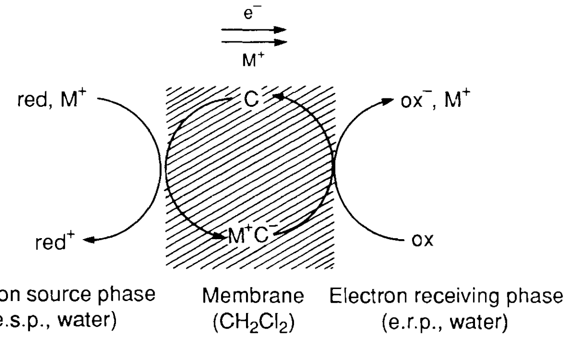

Fig. 1 Three-phase oxidation and reduction reactions. Co-transport of electrons and cations across a liquid membrane, mediated by a lipophilic C–C$^-$ redox system.

There are two possibilities. (*i*) The lipophilic redox system C is prone to a one-electron reduction to give C$^-$: in this case, at the same time as the reduction at the membrane–aqueous reducing phase interface, an M$^+$ cation is taken up to form the ion pair [M$^+$C$^-$], which diffuses to the other side of the membrane; here, C$^-$ is oxidized to C and M$^+$ is released to the aqueous oxidizing phase (see Fig. 1). On the whole, electrons and cations flow from the aqueous reducing phase (electron source phase, e.s.p.) to the aqueous oxidizing phase (electron receiving phase, e.r.p.). (*ii*) The system C is prone to a one-electron oxidation to give C$^+$: in this case, on oxidation, an X$^-$ anion is taken up from the e.r.p., then the [C$^+$X$^-$] ion pair diffuses at the membrane–e.s.p. interface, where C$^+$ is reduced to C and X$^-$ is released to the e.s.p. (see Fig. 2). On the whole, electrons flow from the e.s.p. to the e.r.p. with a counterflow of anions.

Compared to the classical methods, the liquid-membrane procedure may allow selective oxidation and reduction reactions, *i.e.* an oxidizing agent may be able to discriminate among a series of reducing agents (and, *vice versa*, a reducing agent can discriminate among a mixture of oxidizing agents). In principle,

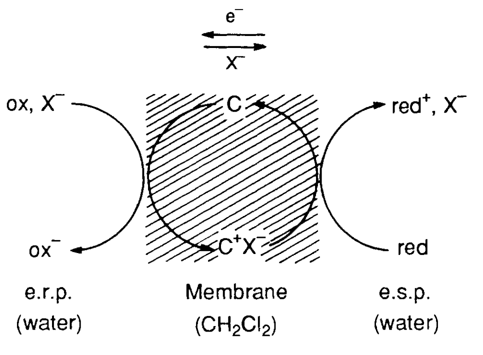

Fig. 2 Three-phase oxidation and reduction reactions. Cross-transport of electrons and anions across a liquid membrane, mediated by a lipophilic C–C$^+$ redox system.

this goal could be achieved by choosing a redox system with an appropriate value of the electrode potential: only ox reagents having E_{ox} larger than E_c can be reduced and, conversely, only red reagents having E_{red} lower than E_c can be oxidized; this should be a thermodynamic control of the three-phase redox process. Even more interesting, if the rate of electron exchange between the redox system in the membrane and the aqueous redox agent at the membrane–water interface varies with the type of ox or red reagents, a further element of selectivity, kinetic in nature, is introduced. In any case, the redox system to be used as a carrier should be able to exchange electrons under two-phase conditions according to an uncomplicated and reversible process, possibly monoelectronic. These considerations have suggested, as versatile carriers for the transport of electrons across liquid membranes, transition-metal-centred redox systems, which are prone to one-electron redox change, according to relatively fast and reversible processes.

In previous work we have investigated the e^-/X^- (X = Cl or ClO_4) cross-transport across a CH_2Cl_2 bulk liquid membrane, mediated by metal complexes of a lipophilic version of the tetraaza macrocycle cyclam (*N*-cetylcyclam = 1-hexadecyl-1,4,8,11-tetraazacyclotetradecane), through the redox change $M^{III} \longrightarrow M^{II}$ (M = Ni[6] or Co[7]). In particular, the Ni^{III}–Ni^{II} redox system, which is located in the higher part of the electrochemical scale, discriminated among a broad class of aqueous reducing agents (from Fe^{II} to Cr^{II}). On the other hand, the more cathodic redox couple, Co^{III}–Co^{II}, in the tetraazamacrocyclic environment, was used to discriminate some aqueous oxidizing agents, including Ce^{IV} and Fe^{III}. Metal(II,III) *N*-cetylcyclam systems are thought to exchange electrons with the chosen aqueous redox agent, at the membrane–aqueous phase interface, through an X bridge, according to an inner-sphere mechanism. In particular, it has been hypothesized that the ability of dichloro(1-hexadecyl-1,4,8,11-tetraazacyclotetradecane)nickel(III) chloride to discriminate among metal-centred (*e.g.* Fe^{II}) and non-metal-centred aqueous reducing agents (*e.g.* I^-), at the membrane–e.s.p. interface, derives from the possibility to form or not X bridges.[6]

We now extend the investigation of cross-membrane oxidation and reduction reactions by looking at electron carriers other than metal complexes of the lipophilic version of cyclam, presenting different features and possibly introducing further elements of selectivity. In particular, we have chosen the very classical $[Fe^{II,III}(bipy)_3]^{2+,3+}$ redox system (bipy = 2,2′-bipyridine). In order to satisfy the solubility requirements of the electron carrier (solubility in the liquid membrane, *e.g.* CH_2Cl_2; insolubility in water), we did not use complexes of bipy, but those of a more lipophilic and hydrophobic derivative obtained by appending Bu^t groups at the 4,4′ positions, *i.e.* 4,4′-di-*tert*-butyl-2,2′-bipyridine, L. Tris(2,2′-bipyridine)metal complexes undergo electron transfer according to an outer-sphere mechanism. We were interested to determine whether and to what extent different electron-transfer mechanisms could affect the rate of two- and three-phase redox processes.

Experimental

*Synthesis of Tris(4,4′-di-*tert*-butyl-2,2′-bipyridine)iron(II) Perchlorate.*—A solution of $(NH_4)_2Fe(SO_4)_2 \cdot 6H_2O$ (1 mmol) in water (25 cm^3) was added dropwise to a boiling ethanolic solution (50 cm^3) containing 4,4′-di-*tert*-butyl-2,2′-bipyridine (3.3 mmol).[8] Then, aqueous 1 mol dm^{-3} $NaClO_4$ (20 cm^3) was added dropwise to the hot, stirred, red solution: a red precipitate formed, which was recrystallized from absolute ethanol. Yield: 980 mg (93%) (Found: C, 61.10; H, 7.05; N, 7.80. Calc. for $C_{54}H_{72}Cl_2FeN_6O_8$: C, 61.20; H, 6.85; N, 7.95%). **CAUTION**: perchlorate salts of metal complexes are explosive. Due caution should be employed when handling them and, in particular, such compounds should never be heated as solids.

Electrochemical and Spectrophotometric Investigations.—The $E_{\frac{1}{2}}$ value associated with the half-reaction $[Fe^{III}L_3][ClO_4]_3 + e^- \longrightarrow [Fe^{II}L_3][ClO_4]_2 + ClO_4^-$ [in CH_2Cl_2, 0.1 mol dm^{-3} NBu_4ClO_4 (C. Erba, Milan, polarographic grade), at 25 °C] was determined through voltammetry studies, using a conventional three-electrode cell. A silver wire was used as a pseudo-reference electrode, calibrated using ferrocene as an internal standard. A PAR model 273 potentiostat/galvanostat, driven by an IBM AT personal computer, was used. UV–VIS spectra of aqueous and dichloromethane solutions were measured by using an Hewlett-Packard 8452A diode-array spectrophotometer or a Cary 2300 (Varian) apparatus.

Two-phase Redox Processes.—Two-phase redox processes were performed in a stoppered 1 cm quartz cuvette, filled with a CH_2Cl_2 solution (2.0 cm^3) of the lipophilic redox agent ($[Fe^{II}L_3][ClO_4]_2$ or $[Fe^{III}L_3][ClO_4]_3$) and an aqueous solution (1.0 cm^3) containing the appropriate oxidizing or reducing agent. Dichloromethane solutions of $[Fe^{III}L_3][ClO_4]_3$ were prepared through two-phase oxidation by excess of Ce^{IV} of a solution of $[Fe^{II}L_3][ClO_4]_2$. The cuvette fitted the HP 89054A thermostattable cell holder, through which water thermostatted at 25.00 ± 0.05 °C was circulated. The beam of light passed through the CH_2Cl_2 layer before being dispersed onto the diode array of the HP 8452A spectrophotometer. The organic layer was magnetically stirred using the HP 89055 stirring module, mounted inside the base of the thermostattable cuvette holder, which was driven by compressed air. We could not determine the rotation rate of the magnetic bar, but it can be assumed that the rate was constant for all the experiments carried out. The rate of a given two-phase redox experiment (*e.g.* the oxidation of 5×10^{-4} mol dm^{-3} $[Fe^{II}L_3][ClO_4]_2$ by an aqueous solution 0.01 mol dm^{-3} in Ce^{IV}, 1 mol dm^{-3} in $HClO_4$ and 1 mol dm^{-3} in $NaNO_3$; volumes of the two layers, 2.0 and 1.0 cm^3, respectively) was found to be constant over a series of experiments periodically performed as a test: a change of the stirring rate would affect drastically the rate of the two-phase chemical process. The procedure employed allowed us to follow the progress of the two-phase redox change, through periodic computer-controlled measurement of the spectra of the lipophilic chromophore, in an automated way. Blank experiments (no redox agent in the aqueous layer) showed that the deuterium lamp light beam passing through the sample during the spectral measurement did not cause any photochemical degradation of the $[Fe^{II}L_3][ClO_4]_2$ and $[Fe^{III}L_3][ClO_4]_3$ complexes.

Three-phase Oxidation and Reduction Experiments.—For electron-transport experiments a V-shaped glass cell was used.[6] In this vessel the two aqueous layers (e.s.p. and e.r.p., 30 cm^3 each) were separated by a CH_2Cl_2 layer of 30 cm^3 (the bulk liquid membrane) and by a glass wall. The membrane, 5×10^{-4} mol dm^{-3} in $[Fe^{II}L_3][ClO_4]_2$, was magnetically stirred at 200 revolutions min^{-1}. The two aqueous layers were mechanically stirred by two glass rods driven by twin electrical motors, at a constant rate (200 revolutions min^{-1}). During the transport experiments, dinitrogen saturated in CH_2Cl_2 flowed in both

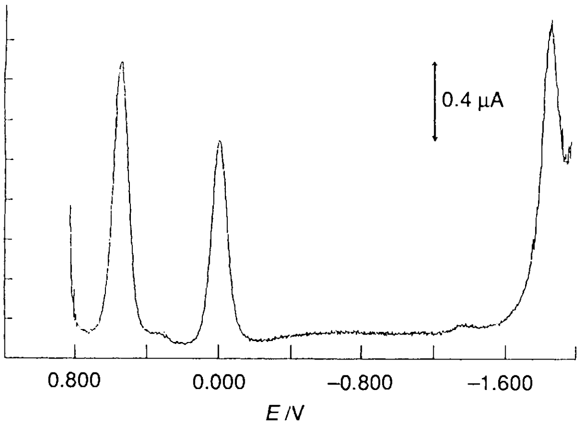

Fig. 3 Differential-pulse voltammetry profile of a CH_2Cl_2 solution 5×10^{-4} mol dm^{-3} in $[Fe^{II}L_3][ClO_4]_2$, 5×10^{-4} mol dm^{-3} in ferrocene and 0.1 mol dm^{-3} in NBu_4ClO_4, at 25 °C. The more anodic peak refers to the half-reaction $[Fe^{II}L_3][ClO_4]_2 + ClO_4^- \longrightarrow [Fe^{III}L_3][ClO_4]_3 + e^-$.

arms of the cell. The progress of the three-phase oxidation and reduction reaction was monitored by syringing out, at selected time intervals, portions of the e.s.p. or e.r.p. aqueous layers (about 200 μl, to fill a 1 mm quartz cuvette) and measuring the spectrum of the redox agent of interest. After each measurement, the aqueous portion was returned to the e.r.p. or e.s.p. Three-phase experiments were carried out in a room thermostatted at 25 ± 1 °C.

Results and Discussion

Choice of the Electron Carrier.—Being interested to use as an electron carrier a redox system able to exchange electrons through the outer-sphere mode, we looked at the classical $[Fe^{II}(bipy)_3][ClO_4]_2$ complex: it undergoes a reversible one-electron oxidation process to give a fairly stable iron(III) complex at a moderately positive potential both in water ($E° = 1.11$ V *vs.* NHE)[9] and in non-aqueous polar solvents.[10] The complex $[Fe^{II}(bipy)_3][ClO_4]_2$ itself is lipophilic enough to dissolve in CH_2Cl_2 (the medium to be used as a membrane in the electron-transport experiments). However, if the resulting red solution is equilibrated with an aqueous layer the complex partitions between the two phases. Charging the aqueous layer with $NaClO_4$ (or $HClO_4$) pushes the iron(II) complex into the organic phase: in the presence of an aqueous layer 1 mol dm^{-3} in $HClO_4$, 99% or more of the $[Fe^{II}(bipy)_3][ClO_4]_2$ resides in an equal volume of CH_2Cl_2. However, if the red dichloromethane layer is equilibrated with a 1 mol dm^{-3} $HClO_4$ aqueous layer containing Ce^{IV} the organic phase is decolorized, whereas the aqueous phase becomes green. The green colour is that of the $[Fe^{III}(bipy)_3]^{3+}$ species, obtained through oxidation of the iron(II) complex by Ce^{IV}; this species, due to its higher electrical charge, prefers to leave the poorly polar CH_2Cl_2 medium and is completely transferred to the aqueous phase. Increasing the $HClO_4$ concentration in the aqueous layer reduces, but does not prevent, the CH_2Cl_2-to-water transfer of the trivalent complex. Thus, we changed to a bipyridine molecule presenting more pronounced lipophilic features. In particular, we considered the ligand 4,4′-di-*tert*-butyl-2,2′-bipyridine (L). The aliphatic shell of the six surrounding Bu^t groups makes the complexes of Fe^{II} and Fe^{III} hydrophobic enough to be confined to the organic layer and to work properly as carriers. The $[Fe^{II}L_3][ClO_4]_2$ complex does not partition even in pure water. Moreover, on oxidation under two-phase conditions of the dichloromethane solution of the $[Fe^{II}L_3][ClO_4]_2$ complex, using an equal volume of an aqueous solution of Ce^{IV} in 1 mol dm^{-3} $HClO_4$, the organic phase turns green: the aqueous oxidizing solution was carefully removed, the CH_2Cl_2 layer washed with three portions of 1 mol dm^{-3} $HClO_4$, then an aqueous solution of a reducing agent was added (*e.g.* Fe^{II} in 1 mol dm^{-3} $HClO_4$) and the two layers equilibrated (by shaking): the organic phase again has the original intense red colour, due to one-electron reduction of the iron(III) complex. Measurement of the visible spectra of the CH_2Cl_2 solution before and after the two-phase oxidation and reduction treatment indicated that 100% of the iron(II) complex was present at the end of the experiment and that, after oxidation, $[Fe^{III}L_3][ClO_4]_3$ was not released to the aqueous layer (1 mol dm^{-3} in $HClO_4$).

The oxidation and reduction behaviour of the $[Fe^{II}L_3][ClO_4]_2$ complex in CH_2Cl_2 solution (0.1 mol dm^{-3} in NBu_4ClO_4) was investigated using voltammetric techniques: Fig. 3 shows the differential-pulse voltammetry profile obtained using a platinum microsphere as a working electrode (pulse amplitude 25 mV, potential scan rate 5 mV s^{-1}); the middle peak refers to the one-electron oxidation of ferrocene, which was added to the solution to calibrate the silver-wire pseudo-reference electrode. The iron(II) complex undergoes a reversible one-electron oxidation at 0.55 V *vs.* the reference couple. Moreover, a one-electron reduction process takes place at a very negative potential, immediately followed by the cathodic discharge.

Two-phase Redox Experiments.—Oxidation of $[Fe^{II}L_3][ClO_4]_2$. In order to assess the conditions for the three-phase oxidation and reduction reactions and, in particular, to choose appropriate aqueous reactants, two-phase experiments were carried out. It has been mentioned in the preceding paragraph that on shaking a CH_2Cl_2 layer containing $[Fe^{II}L_3][ClO_4]_2$ with an aqueous layer containing Ce^{IV} (1 mol dm^{-3} in $HClO_4$) the Fe^{II}-to-Fe^{III} oxidation takes place, under two phase conditions. This would imply that the electrochemical scales of interest to this work, that for aqueous solutions (potentials *vs.* NHE) and that for CH_2Cl_2 solutions (potentials *vs.* ferrocenium–ferrocene) should be juxtaposed in such a way that the potential ascribed to the Ce^{IV}–Ce^{III} couple in 1 mol dm^{-3} $HClO_4$ ($E° = 1.70$ V *vs.* NHE) lies distinctly above that ascribed to the half-reaction $[Fe^{III}L_3][ClO_4]_3 + e^- \longrightarrow [Fe^{II}L_3][ClO_4]_2 + ClO_4^-$ ($E = 0.55$ V *vs.* ferrocenium–ferrocene).* However, the use of perchloric acid as an aqueous background presents some drawbacks: (*i*) the solubility of the cerium(IV) source, anhydrous cerium(IV) sulphate, in 1 mol dm^{-3} $HClO_4$, or even more concentrated, is quite low ($\approx 7 \times 10^{-3}$ mol dm^{-3}) and, in three-phase experiments, it would be useful to operate at higher concentrations of the oxidizing agent; (*ii*) the two-phase oxidation of $[Fe^{II}L_3][ClO_4]_2$ in the presence of aqueous $HClO_4$ is rather slow (see below), whereas fast redox processes at the water–dichloromethane interface are required to carry out oxidation and reduction reactions under three-phase conditions. The solubility of the cerium(IV) salt in aqueous HNO_3 is much higher, but, on equilibration with a CH_2Cl_2 solution of $[Fe^{II}L_3][ClO_4]_2$, the iron(III) complex precipitates at the water–dichloromethane interface. The cerium(IV) salt is fairly soluble in aqueous H_2SO_4, but its solution does not oxidize $[Fe^{II}L_3][ClO_4]_2$ under two-phase conditions, probably due to a thermodynamic effect: the potential associated with the Ce^{IV}–Ce^{III} couple is much lower in aqueous sulphuric acid than in aqueous perchloric acid (1.44 V *vs.* NHE in 0.5 mol dm^{-3} H_2SO_4) and may lie below that associated with the half-reaction $[Fe^{III}L_3]$-

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* The electrochemically determined potential refers to a CH_2Cl_2 solution 0.1 mol dm^{-3} in NBu_4ClO_4. On the contrary, in two- and three-phase experiments, no NBu_4ClO_4 was added to the CH_2Cl_2 layer. The concentration of ClO_4^- in a CH_2Cl_2 layer in equilibrium with an aqueous layer 1 mol dm^{-3} in ClO_4^- can be calculated by using the partition coefficient reported by Abraham and Liszi:[11] log *K*(water/dichloromethane) = 1.8. Thus, through the Nernst equation, an actual potential of 0.60 V can be calculated. All two- and three-phase processes involving the $[Fe^{III}L_3][ClO_4]_3$–$[Fe^{II}L_3][ClO_4]_2$ redox couple described in this paper should be interpreted in terms of the corrected potential.

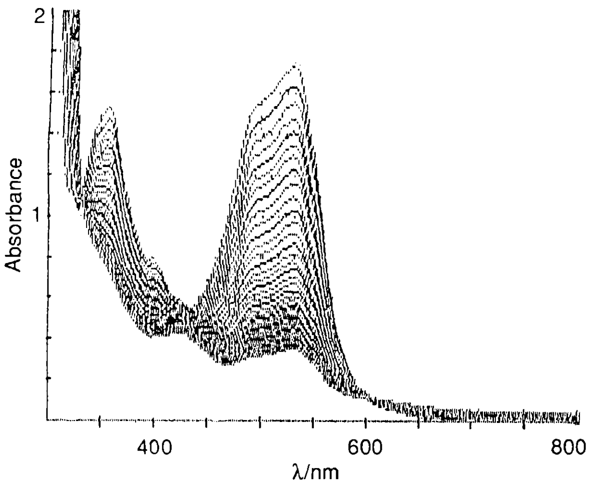

Fig. 4 Two-phase oxidation of $[Fe^{II}L_3][ClO_4]_2$ (5×10^{-4} mol dm^{-3}, in a CH_2Cl_2 solution) by an aqueous solution 7×10^{-3} mol dm^{-3} in Ce^{IV}, 1 mol dm^{-3} in $HClO_4$ and 1 mol dm^{-3} in $NaNO_3$. Spectra were taken every 5 min, on the magnetically stirred CH_2Cl_2 layer (2 cm^3), covered by 1 cm^3 of the aqueous oxidizing solution.

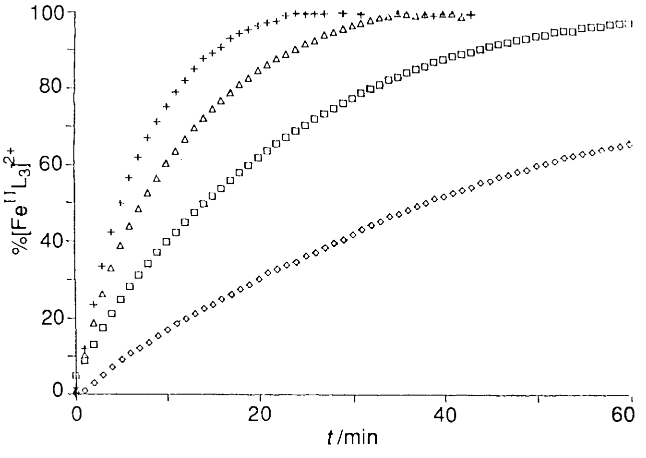

Fig. 5 Two-phase reduction of $[Fe^{III}L_3][ClO_4]_3$ (5×10^{-4} mol dm^{-3}, in a CH_2Cl_2 solution) by 10^{-2} N aqueous reducing agents. The percentage concentration of the reduced complex $[Fe^{II}L_3][ClO_4]_2$ in the CH_2Cl_2 layer, formed during the experiment, was calculated from the intensity of the band at 530 nm. Reducing agents: NO_2^- (+), $[Fe^{II}(CN)_6]^{4-}$ (△), Fe^{2+} (□) and SO_3^{2-} (◇).

$[ClO_4]_3 + e^- \longrightarrow [Fe^{II}L_3][ClO_4]_2$, for the two juxtaposed electrochemical scales. We found that an acidic mixture of ClO_4^- and NO_3^- anions is the best medium in which to perform the two-phase oxidation of $[Fe^{II}L_3][ClO_4]_2$: the solubility of the cerium(IV) salt is high, no precipitate is formed at the water–CH_2Cl_2 interface, the two-phase oxidation of $[Fe^{II}L_3][ClO_4]_2$ is fast, and, in particular, its rate increases with the concentration of NO_3^- present in the aqueous layer.

In order to quantify the kinetic aspects of the two-phase oxidation process, the following experiments were made: a quartz cuvette (1 cm optical path) was filled with a CH_2Cl_2 solution (2 cm^3) 5×10^{-4} mol dm^{-3} in $[Fe^{II}L_3][ClO_4]_2$ and with an aqueous solution (1 cm^3) 7×10^{-3} mol dm^{-3} in Ce^{IV}, 1 mol dm^{-3} in $HClO_4$, and x mol dm^{-3} in $NaNO_3$ ($0 < x < 1$). The organic layer was magnetically stirred at a constant rate and its spectra were recorded at selected time intervals. Fig. 4 reports, as an example, the family of spectra, taken every 5 min, for the experiment in which the aqueous layer was 1 mol dm^{-3} both in $HClO_4$ and $NaNO_3$. The intensity of the bands at 360 and 530 nm [typical of the iron(II) chromophore] decreased progressively, due to the oxidation to the trivalent state. On the other hand, a less-intense band at 426 nm appears and progressively increases, due to the formation of $[Fe^{III}L_3][ClO_4]_3$ in the CH_2Cl_2 layer. The two-phase redox process can be described by equation (1). Under the previously mentioned experimental conditions, the oxidation of $[Fe^{II}L_3][ClO_4]_2$(non-aq) is complete in about 3 h. Decreasing the nitrate concentration in the aqueous phase decreases the rate of the two-phase reaction progressively. In particular, at nil concentration of NO_3^-, *i.e.* in pure 1 mol dm^{-3} $HClO_4$, after 3 h only 25% of the iron(II) complex has been oxidized under two-phase conditions.

$$Ce^{IV}(aq) + ClO_4^-(aq) + [Fe^{II}L_3][ClO_4]_2(\text{non-aq}) \longrightarrow Ce^{III}(aq) + [Fe^{III}L_3][ClO_4]_3(\text{non-aq}) \quad (1)$$

Reduction of $[Fe^{III}L_3][ClO_4]_3$. Prior to the electron transport (three-phase) experiments, we wanted to explore the processes which occur at the other side of the membrane, performing the reduction of the $[Fe^{III}L_3][ClO_4]_3$ complex under two-phase conditions. It has been mentioned before that the pale green dichloromethane layer of $[Fe^{III}L_3][ClO_4]_3$ can be reduced by equilibration with an aqueous acidic solution of Fe^{II}, to produce the intense red layer of $[Fe^{II}L_3][ClO_4]_2$. This finding permits a better assessment of the two electrochemical scales relevant to this work, *i.e.* that in water and that in dichloromethane. In particular, the potential associated with the half-reaction $[Fe^{III}L_3][ClO_4]_3 + e^- \longrightarrow [Fe^{II}L_3][ClO_4]_2 + ClO_4^-$ should lie between that of the Ce^{IV}–Ce^{III} couple (1.70 V *vs.* NHE, in 1 mol dm^{-3} $HClO_4$) and that of the Fe^{III}–Fe^{II} couple ($E° = 0.77$ V). This implies that all the reducing agents whose potential (intended as the potential of the reduction half-reaction) is lower than that associated with the redox change $Fe^{III} \longrightarrow Fe^{II}$ should be able to reduce the $[Fe^{III}L_3][ClO_4]_3$ species under two-phase conditions. This happens and, in particular, reduction takes place on equilibration of a CH_2Cl_2 solution of $[Fe^{III}L_3][ClO_4]_3$ with aqueous solutions 0.1 N in the following reducing agents: NO_2^- [solution buffered at pH 7, 1 mol dm^{-3} $NaClO_4$; $NO_3^- + 2e^- + H_2O \longrightarrow NO_2^- + 2OH^-$; $E°$(pH 7) = 0.51 V]; $[Fe^{II}(CN)_6]^{4-}$ (solution buffered at pH 7, 1 mol dm^{-3} in $NaClO_4$, $E° = 0.36$); SO_3^{2-} [solution buffered at pH 10, 1 mol dm^{-3} in $NaClO_4$; $SO_4^{2-} + 2e^- + H_2O \longrightarrow SO_3^{2-} + 2OH^-$; $E°$(pH 10) = −0.699 V]. Also in this case, redox experiments were performed in a spectrophotometric cuvette, which was typically filled with a CH_2Cl_2 solution (2.0 cm^3) 5×10^{-4} mol dm^{-3} in $[Fe^{III}L_3][ClO_4]_3$ and an aqueous solution (1.0 cm^3) 0.1 N in the reducing agent, 1 mol dm^{-3} in $NaClO_4$ (or $HClO_4$ in the case of Fe^{II}) and adjusted to a given pH, as described before. The progress of the two-phase reduction of $[Fe^{III}L_3][ClO_4]_3$ was monitored through the formation and increase of the typical bands of the red $[Fe^{II}L_3][ClO_4]_2$ chromophore.

Fig. 5 reports a plot of the percentage of $[Fe^{II}L_3][ClO_4]_2$ formed in the CH_2Cl_2 layer (calculated from the ratio of the absorbance of the band at 530 nm to its limiting value) *vs.* time. The rate of the two-phase redox process (expressed by the slope of the linear portion of each % *vs.* time profile) varies with the nature of the reducing agent employed. Noticeably, the sequence of the rates $NO_2^- > [Fe^{II}(CN)_6]^{4-} > Fe^{2+} > SO_3^{2-}$ does not correlate with the sequence of the corresponding reduction potential. At this stage the rate sequence cannot be interpreted on a mechanistic basis. However, it anticipates the possibility to perform selective oxidation and reduction reactions, mediated by the membrane-dissolved $[Fe^{II}L_3][ClO_4]_2$–$[Fe^{III}L_3][ClO_4]_3$ redox system.

It should be noted that, in contrast to the behaviour of the parent $[Fe^{III}(bipy)_3][ClO_4]_3$ complex, which in aqueous solution is slowly reduced by water to restore the divalent species,[12] a dichloromethane solution of $[Fe^{III}L_3][ClO_4]_3$ in equilibrium with an aqueous layer is quite stable and after 1 d less than 5% of the trivalent complex has been reduced (spectrophotometrically determined). Interestingly, fast reduction of $[Fe^{III}L_3][ClO_4]_3$ to $[Fe^{II}L_3][ClO_4]_2$ takes place if the

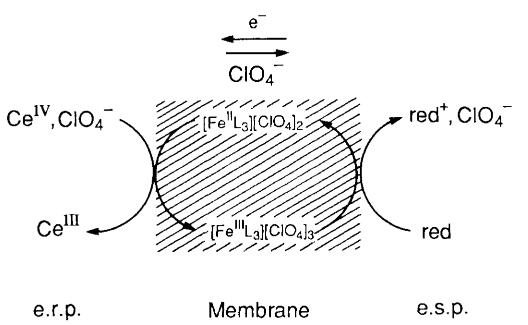

Fig. 6 General scheme for the three-phase oxidation and reduction reaction between Ce^{IV} and a reducing agent red (*e.g.* Fe^{II}), mediated by the membrane-dissolved $[Fe^{II}L_3][ClO_4]_2$–$[Fe^{III}L_3][ClO_4]_3$ redox system. Electrons are transported by $[Fe^{II}L_3][ClO_4]_2$ from the e.s.p. to the e.r.p. and ClO_4^- ions are transported by $[Fe^{III}L_3][ClO_4]_3$ from the e.r.p. to the e.s.p.

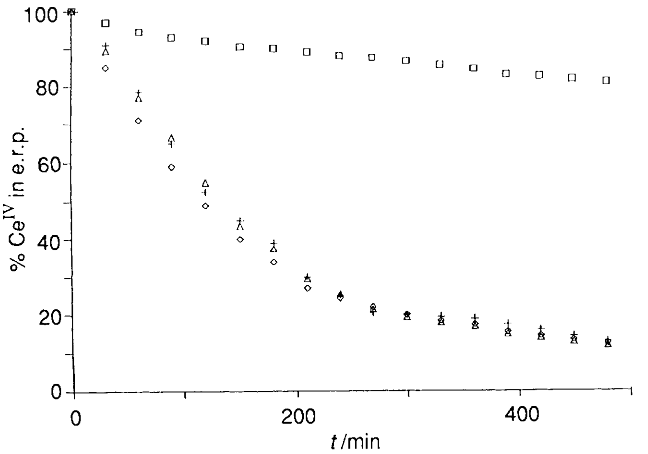

Fig. 7 Concentration profiles for the three-phase reduction of 0.01 mol dm^{-3} Ce^{IV} by various 0.1 N reducing agents, present in excess. Reducing agents: SO_3^{2-} (□), NO_2^- (+), Fe^{2+} (△) and $[Fe^{II}(CN)_6]^{4-}$ (◇).

CH_2Cl_2 layer is equilibrated with aqueous 1 mol dm^{-3} NaOH (instantaneously, on shaking). The kinetic investigation in the spectrophotometric cuvette indicated a rate comparable to that observed for the two-phase reduction by $[Fe^{II}(CN)_6]^{4-}$. This two-phase reaction is intriguing, in particular if one assumes that the reduction of the $[Fe^{III}L_3][ClO_4]_3$ complex by $H_2O(OH^-)$ takes place at the CH_2Cl_2–water interface. If this is true, it may be possible to perform fast oxidation of water under three-phase conditions by any aqueous oxidizing agent able to oxidize the membrane dissolved $[Fe^{II}L_3][ClO_4]_2$ complex (*i.e.* Ce^{IV}). However, two-phase reduction does not take place if the aqueous layer, 1 mol dm^{-3} in NaOH, is made also 1 mol dm^{-3} in $NaClO_4$. This indicates that the reduction process described previously does not occur at the CH_2Cl_2–water interface, but takes place *inside* the organic phase, probably after OH^- has replaced one of the ClO_4^- counter ions of the $[Fe^{III}L_3][ClO_4]_3$ species, due to a concentration effect.* In the presence of an equal amount of ClO_4^-, the much more hydrated hydroxide ion is not extracted into the CH_2Cl_2 layer (to replace the counter ions of the trivalent complex) and no reduction occurs.

Three-phase Redox Processes (*Electron-Transport Experiments*).—Previous preliminary two-phase redox experiments have indicated that oxidation and reduction reactions could be carried out under three-phase conditions, using the $[Fe^{II}L_3][ClO_4]_2$–$[Fe^{III}L_3][ClO_4]_3$ redox system as an electron carrier, in which Ce^{IV} oxidizes a collection of reducing agents of varying nature and strength. On the basis of the two-phase experiments on the reduction of $[Fe^{III}L_3][ClO_4]_3$, one could expect that the three-phase process proceeds in a selective way, *i.e.* the strong and typically non-selective oxidizing agent Ce^{IV} discriminates among a series of reducing agents. Electron-transport experiments were carried out in a V-shaped glass vessel, as described in the Experimental section. In the first series of experiments, the aqueous oxidizing layer (e.r.p.) was 0.01 mol dm^{-3} in Ce^{IV}, 2.5 mol dm^{-3} in $HClO_4$ and 0.5 mol dm^{-3} in HNO_3; the reducing aqueous phase (e.s.p.) was 0.1 N in one of the reducing agents tested in two-phase experiments, 1 mol dm^{-3} in (H,Na)ClO_4, and adjusted to the desired pH, when required. In particular, the aqueous background in the e.s.p., for each three-phase process, was the same as described for two-phase experiments (see above). To monitor the occurrence and progress of the electron transport, portions of the aqueous oxidizing layer were withdrawn by a syringe at selected time intervals and transferred to a cuvette to measure the UV–VIS spectrum. It was observed that the intensity of the absorption band of Ce^{IV}, at 300 nm, using for instance Fe^{2+} as a reducing agent, decreased progressively to reach, after 8 h, 10% of its initial value. In a blank experiment, in which e.r.p. and e.s.p. were made up as described before, but the liquid membrane did not contain anything, the intensity of the band of Ce^{IV} was found to decrease by less than 5% during the same time period, probably due to the reduction of Ce^{IV} by water. The above evidence indicates that the three-phase oxidation of Fe^{II} by Ce^{IV} takes place, according to the mechanism described in Fig. 6 (red = Fe^{II}, red$^+$ = Fe^{III}).

According to the above general scheme, the reduced form of the carrier, $[Fe^{II}L_3][ClO_4]_2$, transports electrons from the e.s.p. to the e.r.p, whereas, to maintain electroneutrality in the membrane, the oxidized carrier, $[Fe^{III}L_3][ClO_4]_3$, transports ClO_4^- ions from the e.r.p. to the e.s.p. (due to the much greater concentration and to the lower hydration energy,[11] it is believed that extraction of ClO_4^- into the membrane strongly predominates over NO_3^- extraction; the possibility of nitrate transport across the liquid membrane, from the e.r.p. to the e.s.p., will be discussed further in the following paragraph). Finally, it should be pointed out that the transport of ClO_4^- is postulated, not demonstrated: the concentration level of the anion prevents any analytical determination (notice that 100% reduction of Ce^{IV} should involve a variation of the perchlorate concentration in the e.s.p. from 1.00 to 1.01 mol dm^{-3}).

Fig. 7 reports the transport profiles obtained with the considered reducing agents: the percentage of Ce^{IV} in the e.r.p. has been calculated from the ratio of the current value of the absorbance at 300 nm to the limiting value. Selective behaviour is observed only in the case of the reducing agent SO_3^{2-}, for which the electron transport appears particularly slow. All the other reducing agents investigated, NO_2^-, $[Fe^{II}(CN)_6]^{4-}$ and Fe^{II}, are not discriminated by Ce^{IV} under the chosen three-phase conditions, in apparent contrast with the results of the two-phase experiments: the transport profiles are coincident within the experimental error and, when the experiment was interrupted (after 8 h), about 90% of Ce^{IV} had been reduced for each of the reducing agents employed. However, failure of the selective behaviour with NO_2^-, $[Fe^{II}(CN)_6]^{4-}$ and Fe^{II} can be accounted for, if one considers the experimental conditions: in this series of transport experiments the limiting redox agent was Ce^{IV} (0.01 mol dm^{-3}), whereas the reducing agent was ten times more concentrated. Thus, it is possible that in the transport experiments with NO_2^-, $[Fe^{II}(CN)_6]^{4-}$ and Fe^{II}, due to the larger concentration, the redox process at the membrane–e.s.p. interface is faster than that at the membrane–e.r.p. interface.

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* Reaction of $[Fe^{III}L_3]^{3+}$ and OH^- in CH_2Cl_2 should produce, at first, H_2O_2. Bulk two-phase experiments were performed in an Erlenmeyer flask, but no H_2O_2 was detected in the aqueous layer after equilibration (chromic acid–diethyl ether method). It is possible that H_2O_2 decomposes instantaneously to give H_2O and O_2. Increase in the dioxygen concentration in the aqueous layer was not investigated.

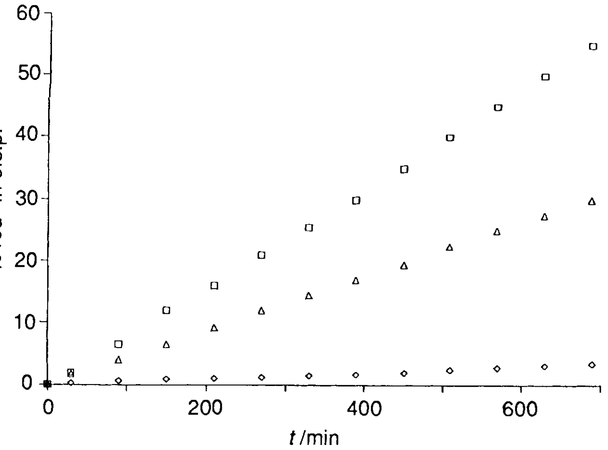

Fig. 8 Concentration profiles for the three-phase oxidation of $[Fe^{II}(CN)_6]^{4-}$ and Fe^{II} (0.01 mol dm^{-3}) by excess of Ce^{IV} (0.10 mol dm^{-3}). The lowest profile (◇) refers to an experiment in which the e.r.p. did not contain Ce^{IV}, but was only 2.5 mol dm^{-3} in $HClO_4$ and 0.5 mol dm^{-3} in HNO_3 and demonstrates the very limited (or not occurring) transport of NO_3^- from the e.r.p. to the e.s.p. (see text). Species: $[Fe^{III}(CN)_6]^{3-}$ (□) and Fe^{3+} (△).

Therefore, the rate-determining step for the three-phase process is that involving reduction of Ce^{IV} by $[Fe^{II}L_3][ClO_4]_2$, which obviously cannot depend upon the nature of the reducing agent. On the other hand, the two-phase reduction of $[Fe^{III}L_3][ClO_4]_3$ by aqueous SO_3^{2-} is so intrinsically slow that, even in the presence of an excess of the sulphite ion, it proceeds at a lower rate than the reduction of Ce^{IV}, thus determining the rate of the overall process.

In order to discriminate reducing agents, one should perform experiments in which the reducing agent is the limiting reagent and the oxidizing agent is present in overwhelming concentration. Therefore, a second series of experiments was carried out in which the e.r.p. was 0.10 mol dm^{-3} in Ce^{IV}, 2.5 mol dm^{-3} in $HClO_4$ and 0.5 mol dm^{-3} in HNO_3;* the membrane was 5×10^{-4} mol dm^{-3} in $[Fe^{II}L_3][ClO_4]_2$; and the e.s.p. was 0.01 mol dm^{-3} in Fe^{II} or $[Fe^{II}(CN)_6]^{4-}$. In this series of experiments the progress of the electron transport was followed by measuring, at selected time intervals, the spectrum of the e.s.p. solution. In the case of $[Fe^{II}(CN)_6]^{4-}$, appearance and progressive increase of the band at 420 nm, ascribed to the $[Fe^{III}(CN)_6]^{3-}$ chromophore, were observed. For the experiment with Fe^{II}, portions of the e.s.p. were added to a standard concentrated solution of HCl and the appearance and increase of an intense band, centred at 344 nm and ascribed to the iron(III) chloro-complex, was recorded.

Fig. 8 shows the transport profiles obtained with $[Fe^{II}(CN)_6]^{4-}$ and Fe^{II} as reducing agents, in which the percent concentration of the oxidized form of the reducing agent in the e.s.p. (red^+) is plotted *vs.* time. Selective behaviour is now observed, the $[Fe^{II}(CN)_6]^{4-}$ ion being oxidized at a rate approximately double that of Fe^{II}. In particular, when the two experiments were interrupted (after nearly 12 h), 55% of $[Fe^{II}(CN)_6]^{4-}$ and almost 30% of Fe^{II} had been oxidized.

At the concentration level employed, it may be that NO_3^- ions, in view of a substantial concentration gradient (0.5–0 mol dm^{-3}), are transported by the membrane-dissolved iron complex, from the e.r.p. to the e.s.p. Due to its oxidizing properties in acidic solution, the NO_3^- ion should be able to oxidize Fe^{II} in the e.s.p. (1 mol dm^{-3} $HClO_4$), simulating an electron transport. Thus, an experiment was made in which the e.r.p., 2.5 mol dm^{-3} in $HClO_4$ and 0.5 mol dm^{-3} in HNO_3, did not contain Ce^{IV}, and the membrane and the e.s.p. were made up as before. The concentration of Fe^{III}, after 12 h, was confined within 3% (see Fig. 8), indicating that transport of NO_3^-, if any, is extremely low and, in any case, does not alter significantly the results of electron-transport experiments mediated by the $[Fe^{II}L_3][ClO_4]_2$–$[Fe^{III}L_3][ClO_4]_3$ redox system.

It should be considered that mass-transfer effects could also play an important role in determining the rate of the three-phase redox processes investigated. However, as the stirring rates have been kept constant for the various runs, mass-transfer rates are considered roughly constant. Thus, the selectivity pattern is to be ascribed chiefly to chemical (kinetic) effects.

The present investigation has further demonstrated that transition-metal complexes may behave as efficient carriers of electrons and anions in membrane-mediated oxidation and reduction reactions and that the kinetic features of the redox processes at the membrane–aqueous phase interface (e.s.p. or e.r.p.) may generate interesting selectivity effects. From the described experiments, it has been possible to draw the conclusions that the rate of the overall three-phase process is determined by that of the slowest of the two-phase processes (rather obvious) and that the slowest step can be chosen by changing the relative concentrations of the aqueous redox reagents in the e.r.p. and in e.s.p. (less obvious).

The lipophilic redox system used as a carrier in the present study has an intrinsically high electrode potential (0.55 V *vs.* ferrocenium–ferrocene in CH_2Cl_2 solution, 0.1 mol dm^{-3} NBu_4ClO_4), thus juxtaposing the more 'oxidizing' part of the aqueous electrochemical scale. As a consequence, the $[Fe^{III}L_3][ClO_4]_3$–$[Fe^{II}L_3][ClO_4]_2$ redox system allows three-phase oxidation and reduction reactions involving a very limited number of oxidizing agents (in practice, only Ce^{IV}) and a large number of reducing agents. This makes it possible to explore selectivity towards reducing agents. Indeed, the electron carrier studied in this work disclosed some interesting kinetic effects. In particular, it is noticeable that the most powerful reducing agent SO_3^{2-} is oxidized at the lowest rate, among the considered reducing agents.†

Comparison with the $[Ni^{III}L'Cl_2]Cl$–$[Ni^{II}L'Cl_2]$ (L' = *N-cetylcyclam*) *Redox System*.—We wished to compare the behaviour of the $[Fe^{III}L_3][ClO_4]_3$–$[Fe^{II}L_3][ClO_4]_2$ system to that of the previously investigated $[Ni^{III}L'Cl_2]Cl$–$[Ni^{II}L'Cl_2]$ system (L' = *N*-cetylcyclam). Both metal(III,II) carriers are situated in the more positive part of the electrochemical scale and may be used to discriminate among aqueous reducing agents. However, a correct comparison cannot be made, since we were not able to perform the same oxidation and reduction process, under three-phase conditions, mediated by the two different carriers. The L' system is quickly oxidized only by persulphate ion, under two-phase conditions. Cerium(IV) cannot be employed as an aqueous oxidizing agent, as it oxidizes the aqueous chloride background, essential for stabilizing the nickel(III) carrier complex. On the other hand, $S_2O_8^{2-}$ does not oxidize $[Fe^{II}L_3][ClO_4]_2$, under two-phase conditions. However, a common reducing agent working with the two membrane-dissolved redox systems exists, namely Fe^{II}. Thus we have performed, under the same experimental conditions (0.1 N oxidizing agent, 10^{-3} mol dm^{-3} carrier, 10^{-2} mol dm^{-3} Fe^{II}) the following two three-phase reactions: (i) $\frac{1}{2}S_2O_8^{2-}$–$[Ni^{II}L'Cl_2]$–

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* The large concentration of acid was used to increase the solubility of cerium(IV) sulphate to a relatively high level (0.1 mol dm^{-3}). The 5:1 ClO_4^-/NO_3^- ratio should prevent nitrate extraction in the organic phase. The same acid background had been also used in the previously described three-phase experiments in which Ce^{IV} was the limiting reagent.

† The thermodynamic aspects of the electron transfer between immiscible solutions (*e.g.* water and dichloroethane) have recently been considered.[13] In particular, it has been shown that the position of equilibrium in a two-phase redox system is dependent on the values of the standard potentials of the couples present in the two phases and also on the interfacial Galvani potential difference. In the present investigation, no attempts were made to determine the Galvani potential. Thus, the interpretation of the results is only qualitative.

Fe^{II} and (ii) Ce^{IV}–$[Fe^{II}L_3][ClO_4]_2$–Fe^{II}. Even in the presence of a certain induction period (probably ascribed to the special kinetic properties of persulphate ion) the oxidation of Fe^{II} in reaction (i) is complete after 7 h; at that time, in the process (ii), only 30% of Fe^{II} has been oxidized. This would indicate that the inner-sphere redox system $[Ni^{II}L'Cl_2]$–$[Ni^{III}L'Cl_2]Cl$ is a much more efficient electron carrier than the outer-sphere redox system $[Fe^{II}L_3][ClO_4]_2$–$[Fe^{III}L_3][ClO_4]_3$. However, further studies on a larger number of systems should be carried out before drawing any sound conclusion about the effect of the inner- or outer-sphere nature of the carrier on the transport efficiency (if it exists).

More interesting observations can be made on the selectivity towards reducing agents displayed by the two redox systems. The $[Ni^{III}L'Cl_2]Cl$ complex can be reduced, under two-phase conditions, only by metal centred reducing agents (which is reasonable, if one hypothesizes that the electron transfer takes place through a chloride ion bridging the two metal centres) and is not reduced, under two-phase conditions, by non-metal systems (*e.g.* I^-). On the contrary, the fully saturated $[Fe^{III}L_3][ClO_4]_3$ species does not discriminate among metal and non-metal centred aqueous reducing agents, being reduced by both classes of reagents. This behaviour is expected for a redox agent exchanging electrons through an outer-sphere mode. Differences in two-phase reaction rates may arise from more subtle kinetic effects, which do not seem directly related to the metallic or non-metallic nature of the aqueous reducing agent, nor to the sign of its electrical charge. Incidentally, among the four aqueous reducing agents investigated here, the two non-metal systems (nitrite and sulphite anions) give the fastest and the slowest two-phase reactions, respectively.

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