

## Transport of Electrons and Sodium Ions through Liquid Membranes Mediated by Platinum Clusters

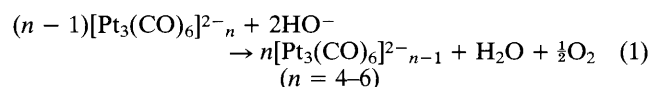
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Using hydroxide and ferricyanide ions as the electron donor and acceptor, respectively, electrons and sodium ions are transported through organic liquid membranes by anionic carbonyl clusters of platinum.

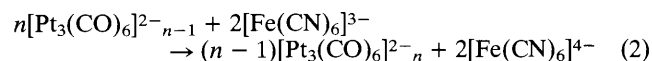
Controlled transport of electrons and alkali metal ions across cell membranes is of fundamental importance in biological processes.<sup>1</sup> Electron transport is known to be accompanied by a pH gradient.<sup>1</sup> A few artificial systems have been reported where the transport of electrons is coupled with that of alkali metal ions.<sup>2</sup> For liquid membranes *i.e.* relatively thick organic barriers, this has been achieved by using redox active molecules such as anthraquinone or nickel bis(dithiolene) in combination with crown ethers.<sup>2,3</sup> Here we report simultaneous transport of electrons and sodium ions in the same direction (symport) through organic liquid membranes. The electron transport is driven by a pH gradient and is based on the redox properties of anionic carbonyl clusters of platinum.

The syntheses of platinum clusters of the general formula  $[\text{Pt}_3(\text{CO})_6]^{2-n}$  ( $n = 1-6$ ) and reactions of some of these clusters with  $\text{HO}^-$  were first reported by Longoni and Chini<sup>4</sup> [eqn. (1)].

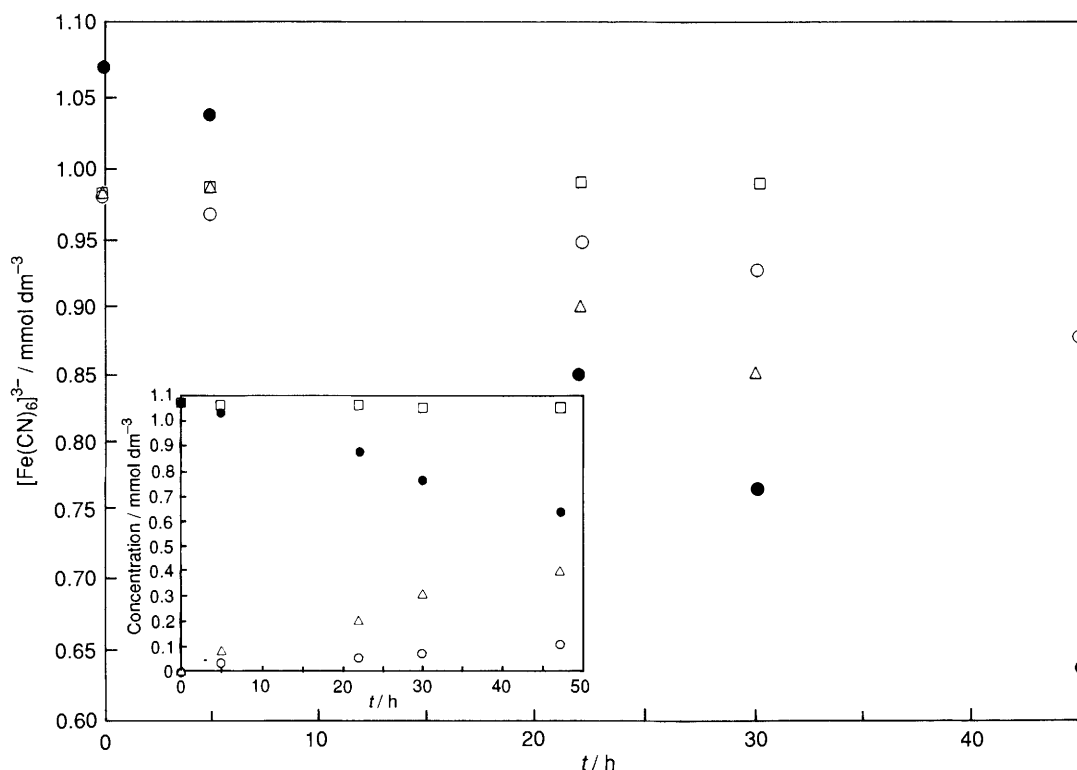
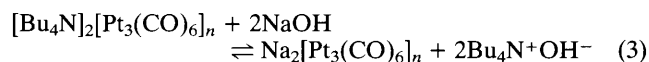


We find that in a two-phase system consisting of a dichloromethane solution of  $[\text{Bu}_4\text{N}]_2[\text{Pt}_3(\text{CO})_6]_{n-1}$  and an aqueous solution of  $\text{Fe}(\text{CN})_6^{3-}$ , clean reduction of ferricyanide and oxidation of the cluster anions take place according to reaction (2). Similarly the reduction of the cluster anions

according to reaction (1) could be effected in a biphasic system with aqueous sodium hydroxide. These reactions are monitored easily and quantified on the basis of the well-established UV-VIS spectra of the cluster anions.<sup>5</sup>

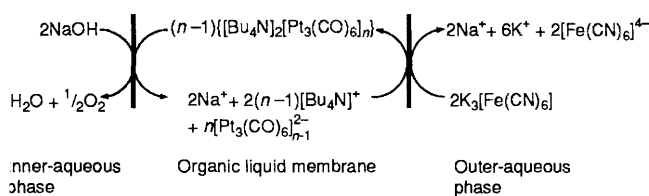


As shown in Scheme 1 use of the cluster anion as a redox catalyst to effect reactions (1) and (2) at the interfaces, should result in the transport of electrons and sodium ions in the same direction. The overall chemical reaction *i.e.* reduction of ferricyanide by hydroxide ion, is thermodynamically favourable and has an approximate standard free energy of  $-25 \text{ kJ mol}^{-1}$ . Although not shown in Scheme 1, the transport of sodium ions is also expected to be facilitated by simple ion-pairing *i.e.* formation of sodium salts of the platinum carbonyls at the interface. Like the tetrabutyl ammonium salts, the sodium salts of the platinum carbonyls are insoluble in water but have limited solubilities in dichloromethane. The rate of transport of sodium ions may be thus faster than that of electrons and would be dependent on the  $\text{Na}^+$  concentration according to equilibrium (3).



**Fig. 1** Reduction of ferricyanide ion with time measured by UV-VIS spectrophotometry. (□), No cluster, NaOH (15 ml,  $0.75 \text{ mol dm}^{-3}$ ), dichloromethane (125 ml); (Δ), as for □ but with  $[\text{Bu}_4\text{N}]_2[\text{Pt}_{12}(\text{CO})_{24}]$  ( $0.0015 \text{ mmol dm}^{-3}$ ); (○), as for Δ but with NaOH (15 ml,  $0.1 \text{ mol dm}^{-3}$ ); (●), n-hexanol (124.5 ml), DMF (0.5 ml), NaOH (15 ml,  $0.1 \text{ mol dm}^{-3}$ ),  $[\text{Bu}_4\text{N}]_2[\text{Pt}_{12}(\text{CO})_{24}]$  ( $0.0015 \text{ mmol dm}^{-3}$ ).

Inset: Changes in concentration of ferricyanide and sodium ions in the outer-aqueous layer with time. n-Hexanol (124.5 ml), DMF (0.5 ml), NaOH (15 ml,  $0.1 \text{ mol dm}^{-3}$ ), (□) and (○), concentrations of ferricyanide and sodium ion, respectively, in the absence of cluster; (●) and (Δ), concentrations of ferricyanide and sodium ions, respectively, with  $[\text{Bu}_4\text{N}]_2[\text{Pt}_{12}(\text{CO})_{24}]$  ( $0.0015 \text{ mmol dm}^{-3}$ ).



The validity of these reasonings has been tested by using two concentric cylindrical glass vessels (diameter 6.5 and 2.5 cm), with NaOH solution (15 ml, 0.1–0.75 mol dm<sup>-3</sup>) in the open-bottom inner vessel and potassium ferricyanide solution (85 ml, 1 mmol dm<sup>-3</sup>) in the outer vessel. Dichloromethane (125 ml) has been used as the intervening liquid membrane. A U-tube cell (300 ml) has also been used and found not to have any significant effect on the experimental findings.

n-Hexanol has also been used as another liquid membrane. Since both the n-butyl and cetyl trimethyl ammonium salts of the cluster anions are totally insoluble in n-hexanol, very small quantities (0.5 ml) of dimethylformamide (DMF) have been added to solubilise the clusters. In these experiments a closed-bottom inner vessel, with the intervening hexanol layer at the top of the separated aqueous layers has been used. The platinum cluster [Bu<sub>4</sub>N]<sub>2</sub>[Pt<sub>12</sub>(CO)<sub>24</sub>] (0.0015 mmol dm<sup>-3</sup>) has been used as the precatalyst for the redox reactions (1) and (2). To facilitate transport across the phase boundaries the lower phases have been magnetically stirred. The extent of ferricyanide reduction and the concentration of transported sodium ions have been measured by UV–VIS and atomic absorption spectrometry, respectively. The volume of outer-aqueous layer that needed to be removed for concentration measurements is small (1 ml), and, therefore, should have no significant effect on the equilibria.

As can be seen from Fig. 1 transport of electrons resulting in the reduction of [Fe(CN)<sub>6</sub>]<sup>3-</sup> is observed for both the organic phases. The rate of transport of electrons is primarily dependent on the nature of the organic phase, and the concentration of hydroxide ions. The higher rate of electron transport in n-hexanol/DMF may be due to relatively better miscibility of this solvent system at the aqueous interfaces, as compared to that of dichloromethane. This is inferred on the basis of Hildebrand solubility parameters, δ (H), of these solvents with values 10.7, 12.1 and 9.7 H, respectively.<sup>6</sup> Presumably an increase in the base concentration enhances the extent of reaction (1) at the inner-phase boundary, resulting in a net increase in the rate of electron transport.

The drop in the concentration of ferricyanide ion in the outer-aqueous layer through ion-pairing, *i.e.* an equilibrium leading to the formation of tetrabutyl ammonium salt of ferricyanide ion, is ruled out. This is established on the basis of UV–VIS spectral changes with isobesticity indicating reduction rather than dilution of the ferricyanide ions. Furthermore, the use of tetrabutyl ammonium chloride of an equivalent molar amount in place of the platinum cluster does not cause any change in the ferricyanide concentration.

In accordance with the mechanism shown in Scheme 1, when moderately strong base (0.1 mol dm<sup>-3</sup>) is used the ratio of the concentrations of transported sodium ions and reduced ferricyanide is found to be approximately one (Fig. 1, inset). Under these conditions the additional transport of sodium ions through passive ion-pairing *i.e.* equilibrium (3), is not noticeable. Contribution owing to equilibrium (3) becomes noticeable for both the liquid membranes when a strong (0.75 mol dm<sup>-3</sup>) sodium hydroxide solution is used. The amount of transported sodium ion far exceeds the amount of reduced ferricyanide. The presence of platinum clusters [Pt<sub>3</sub>(CO)<sub>6</sub>]<sup>2-n</sup> (n = 3–5) in the organic phases in all these experiments is established by time-monitored UV–VIS and IR spectra.<sup>4,5</sup> This also lends support to the proposed mechanism for transport.

In conclusion the redox active anionic clusters of platinum have been shown to be effective mediators for the symport of electrons and sodium ions.

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