PHOTOSENSITIZED ELECTRON TRANSFER REACTIONS IN ORGANIZED INTERFACIAL SYSTEMS*

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Summary

The separation of photoproducts formed in photosensitized electron transfer reactions is essential for efficient energy conversion and storage. The organization of the components involved in the photoinduced process in interfacial systems leads to efficient compartmentalization of the products. Several interfacial systems, *e.g.* lipid bilayer membranes (vesicles), water-in-oil microemulsions and a solid SiO_2 colloidal interface, were designed to accomplish this goal.

An electron transfer across a lipid bilayer membrane leading to the separation of the photoproducts at opposite sides of the membrane is facilitated by establishing a transmembrane potential and organizing the cotransport of cations with specific carriers.

Colloidal SiO_2 particles provide a charged interface that interacts with charged photoproducts. By designing a system that results in oppositely charged photoproducts, a retardation of recombination by the charged interface can be produced. The photosensitized reduction of a neutral acceptor by positively charged sensitizers is described. The reactions are substantially enhanced in the SiO_2 colloid compared with in the homogeneous phase. The effect of the SiO_2 interface is attributed to a high surface potential that results in the separation of the intermediate photoproducts. The quantum yields of the photosensitized reactions are correlated with the interfacial surface potential and the electrical effects of other charged interfaces such as micelles are compared with those of SiO_2.

The possible utilization of the energy stored in the stabilized photoproducts in further chemical reactions is discussed. Special attention is given to the photo-decomposition of water.

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1. Introduction

Reactions in organized media as a means of modeling natural processes are currently an intensive subject of research [1, 2]. Of particular interest is the subject of "artificial photosynthesis", *i.e.* attempts to create a synthetic appara-

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tus that mimics the functions of the natural process [3, 4]. The natural photo-synthetic cycle

$$H_2O + CO_2 \xrightarrow{h\nu} [CH_2O] + O_2 \qquad (1)$$

can be separated into two major parts: a photochemical part, in which visible light is captured and transformed into chemical energy, and a chemical part, in which the stored energy is utilized in a sequence of dark reactions. The process is summarized in the "Z scheme" (Fig. 1). The chloroplast utilizes two photo-systems composed of well-organized pigment molecules. Photoexcitation of these units induces electron transfer reactions that result in the oxidation of water to oxygen and formation of a reduced intermediate (ferredoxin). The reducing power is then used in a set of dark reactions to form carbohydrates from CO_2.

Several approaches to the design of organized and controlled photosensi-tized electron transfer reactions will be discussed. Special emphasis will be given to the utilization of the stored energy in the photodecomposition of water:

$$H_2O \rightarrow H_2 + \tfrac{1}{2}O_2 \qquad (2)$$

The mimicking of photosynthesis with the goal of decomposing water must involve three cooperative elements: (a) a light-capturing entity that is capable of photosensitizing electron transfer reactions; (b) an interfacial barrier that separates the intermediate photoproducts and prevents their recombination; (c) suitable redox catalysts capable of reducing and oxidizing water.

Many synthetic dyes have been used in the photosensitization of electron transfer reactions. In the past few years several promising organometallic com-pounds have been prepared as substitutes for the natural labile chlorophyll. These organometallics include a variety of metals, chelated to bipyridine or porphyrin ligands. The photophysical properties of these sensitizers and their potential use
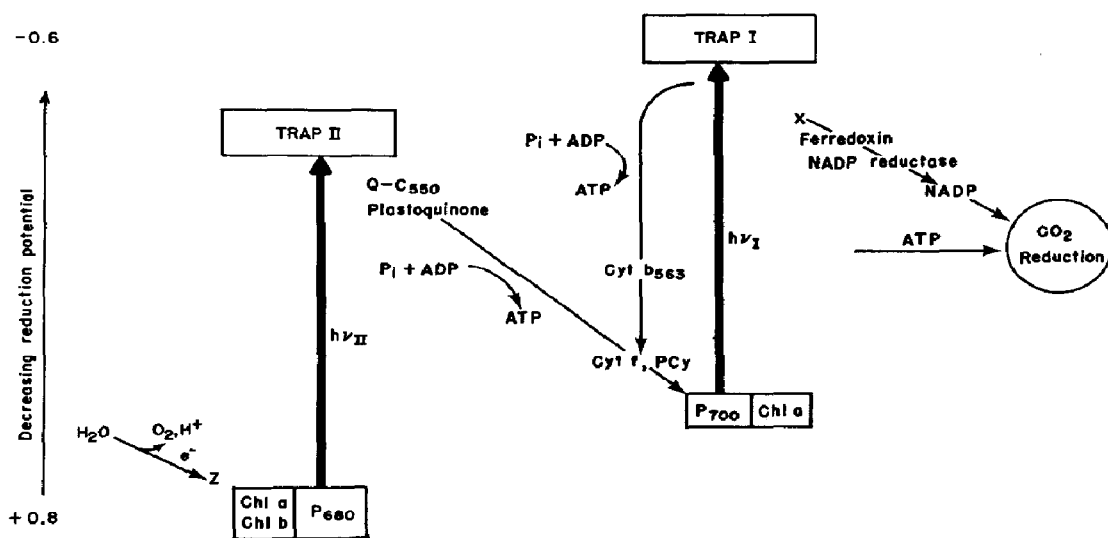

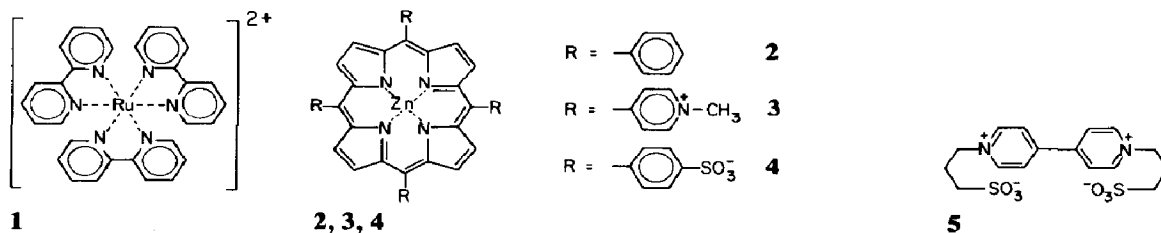Fig. 1. Photosynthetic electron transfer scheme (Z scheme).

Fig. 2. Structural formulae for acceptors, donors and sensitizers: **1**, Ru(bipy)$_3$$^{2+}$; **2**, zinc *meso*-tetraphenylporphyrins; **3**, **4**, water-soluble zinc *meso*-tetraphenylporphyrins; **5**, propyl viologen sulfonate.

in artificial photosynthetic devices have been extensively reviewed [5, 6]. In particular, sensitizers such as *tris*(bipyridine)Ru(II) (Ru(bipy)$_3$$^{2+}$ **1** (Fig. 2)) and zinc porphyrins (such as zinc *meso*-tetraphenylporphyrins **2** or water-soluble derivatives **3** and **4** (Fig. 2)) have been widely explored. Various structural modifications such as hydrophobic substituents and charged headgroups have also been introduced. Thus, control of electrostatic interactions and precise location of the sensitizer in hydrophilic or hydrophobic environments can be achieved.

The storage of energy by means of a photosensitized electron transfer cycle requires a close proximity of the components for efficient quenching of the excited species. However, once the photoproducts are produced, their separation must be assisted and a barrier for their combination must be introduced. Several interfacial systems such as micelles [7, 8], water-in-oil [9] or oil-in-water [10] microemulsions and bilayer membranes [11, 12] (vesicles) provide microenvironments that meet these requirements.

Since these interfaces are usually constructed of charged detergents a diffuse electrical double layer is produced and the interfacial boundary can be characterized by a surface potential. Consequently, electrostatic as well as hydrophilic and hydrophobic interactions of the interfacial system can be designed. We shall review our achievements in organizing photosensitized electron transfer reactions in different microenvironments, and in addition a novel solid–liquid interface provided by colloidal SiO$_2$ particles in an aqueous medium will be discussed as a means of controlling photosensitized electron transfer reactions [13].

2. Photosensitized electron transfer across bilayer membranes

With the knowledge that membranes play an important role in the natural process, we initiated a study in which bilayer phospholipid membranes (vesicles) serve as an artificial structure. For this purpose an electron transfer across the bilayer boundary must be accomplished [14]. The schematic diagram of our system is presented in Fig. 3. In this system an amphiphilic ruthenium complex is incorporated into the membrane wall. An electron donor, ethylenediaminetetraacetic acid (EDTA), is entrapped in the inner compartment of the vesicle, and heptyl viologen (HV^{2+}) as an electron acceptor is introduced into the outer phase. Upon illumination an electron transfer process across the vesicle walls is
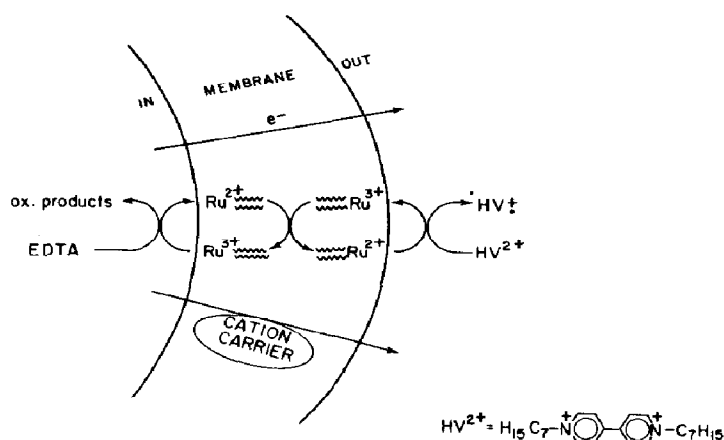
198

MEMBRANE OUT

IN

e⁻

ox. products

EDTA

Ru²⁺   Ru³⁺   HV⁺̇

Ru³⁺   Ru²⁺   HV²⁺

CATION CARRIER

HV²⁺ = H₁₅C₇–N⁺◯–◯N⁺–C₇H₁₅

Fig. 3. A scheme for photosensitized electron transfer across a lipid vesicle wall.

initiated and the reduced acceptor $HV \cdot {}^+$ is produced. The excited sensitizer transfers an electron to HV^{2+} in the primary event. The oxidized sensitizer thus produced oxidizes an Ru^{2+} located at the inner surface of the vesicle and thereby the separation of the intermediate photoproducts is assisted. The further oxidation of EDTA regenerates the sensitizer and consequently the separation of the reduced species $HV \cdot {}^+$ from the oxidized product is achieved. In this system the basic principle of a vectorial electron transfer across a membrane is demonstrated. However, the quantum yield for the reaction is rather low ($\varphi \approx 4 \times 10^{-4}$).

The transmembrane electron transfer was found to be the rate-limiting factor for the overall reaction and the origin of the low efficiency. The electron transfer across the membrane must be followed by cotransport of cations in order to keep charge neutrality. Since the membrane has a low permeability to such cations, the photosensitized reaction might be limited by this effect. Indeed, further elaboration of the vesicle system by including cation carriers can improve the photoinduced reaction. For this purpose hydrophobic cation carriers (ionophores) such as valinomycin (specific for K^+), carbonyl cyanide m-chlorophenyl hydrazone (CCCP) (specific for H^+) and gramicidin (transport agent of K^+, Na^+ and H^+) have been incorporated into the hydrophobic region of the vesicles [16]. The photosensitized electron transfer reaction in the presence of these carriers is enhanced threefold to sixfold, depending on the ionophore (Fig. 4). These results confirm that the cotransport of cations plays an important role in the photosensitized reactions.

In addition to their function in establishing charge neutralization during the photochemical reactions, cations might, by proper organization, even assist the electron transfer via production of a transmembrane potential. Different concentrations of K^+ in the opposite aqueous phases of the lipid bilayer were used to test for this effect. The specific K^+ carrier valinomycin was incorporated into the vesicle walls. Consequently, owing to the concentration difference, a long-lasting transmembrane potential was established. The photosensitized electron transfer reaction appears to be affected by such electric fields (Fig. 4(b)).
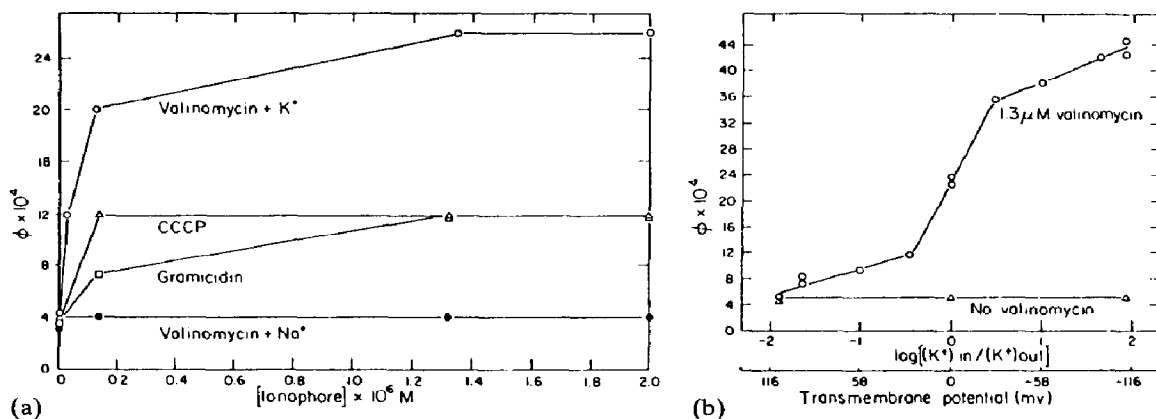
Fig. 4. The effect of ionophores (a) and transmembrane potentials (b) on the quantum yield φ of heptyl viologen reduction in the vesicle system: CCCP, H^+ carrier; valinomycin, K^+ carrier; gramicidin makes the membrane permeable for several cations such as H^+, K^+ and Na^+.
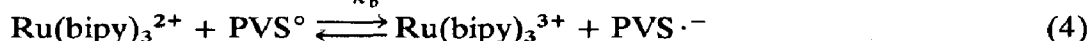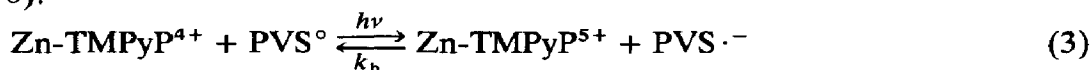
It can be seen that when the ratio $[K^+]_{in}/[K^+]_{out}$ is greater than unity, *i.e.* the interior boundary is negative relative to the exterior, the reaction is enhanced twofold compared with the system without any applied field. Conversely, when the vesicles are designed such that $[K^+]_{in}/[K^+]_{out}$ is less than unity and an opposite potential is formed, the quantum yield is decreased and approaches the value obtained in the absence of any valinomycin [14]. We can see that the combined effects of cation permeability and a transmembrane potential result in an elevenfold enhancement in the photosensitized reduction of HV^{2+}. Thus, proper organization of different components in the lipid bilayer interfacial system can enhance electron transfer reactions and assist the separation of photoproducts across the bilayer.

3. Photosensitized electron transfer reactions in SiO_2 colloids

Colloidal SiO_2 particles in an aqueous suspension provide a solid–liquid interface. The silanol groups on the particle surface are ionized at pH $\geqq 6$. Consequently, the surface of the particle is negatively charged and a diffuse electrical double layer is produced in the vicinity of the solid interface. Because of the negative charges on the particles they repel one another and their agglomeration is prevented. The particles can be used to exert electrostatic repulsive and attractive interactions with the components involved in photosensitized reactions. By means of these interactions a component can be selectively adsorbed to the interface and its recombination with an oppositely charged photoproduct can be retarded.

To achieve such an organization in the system the different components have to be functionalized. Two positively charged sensitizers, $Ru(bipy)_3^{2+}$ **1** or zinc *meso*-tetramethylpyridinium porphyrin (Zn-$TMPyP^{4+}$ **3** (Fig. 2)), that are adsorbed to the SiO_2 interface are used [19]. The zwitterionic dipropylsulfonate-

200

4,4'-bipyridinium 5 (propylviologen sulfonate, PVS°) is used as electron acceptor, and triethylamine (TEA) is introduced as electron donor. Photosensitized electron transfer in these systems results in a rapid production of the viologen radical PVS·⁻. The rates of PVS·⁻ formation in the colloidal SiO_2 systems using the different sensitizers are shown in Fig. 5 and are compared with the analogous reactions in a homogeneous phase. It can be seen that the electron transfer reactions in the SiO_2 colloid are enhanced about tenfold relative to the homogeneous phase, and using Zn-TMPyP⁴⁺ as sensitizer a high quantum yield ($\varphi = 0.35$) is obtained. The enhanced quantum yields in the SiO_2 colloids are ascribed to the control of the electron transfer reaction by means of electrostatic interactions (Fig. 6):

$$\text{Zn-TMPyP}^{4+} + \text{PVS}° \underset{k_b}{\overset{h\nu}{\rightleftharpoons}} \text{Zn-TMPyP}^{5+} + \text{PVS}\cdot^{-} \tag{3}$$

$$\text{Ru(bipy)}_3{}^{2+} + \text{PVS}° \rightleftharpoons \text{Ru(bipy)}_3{}^{3+} + \text{PVS}\cdot^{-} \tag{4}$$

The electron transfer from the excited sensitizer $\text{Ru(bipy)}_3{}^{2+}$ to the neutral electron acceptor results in two oppositely charged photoproducts. The charged interface interacts with these intermediate photoproducts; the oxidized sensitizer is adsorbed at the interface while the reduced negatively charged electron acceptor
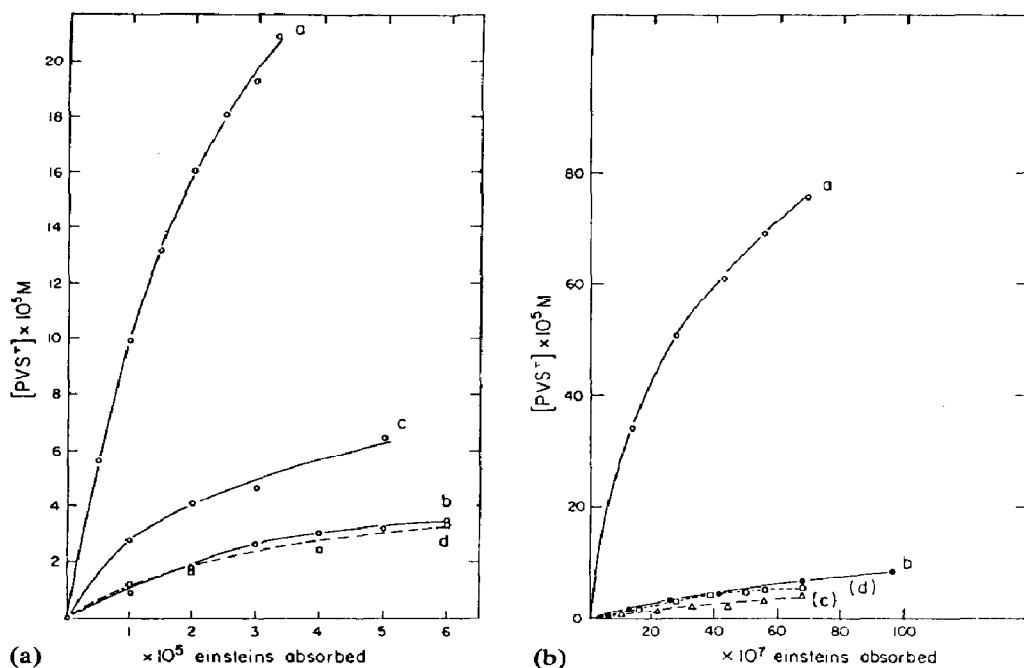

(a)   ×10⁵ einsteins absorbed   (b)   ×10⁷ einsteins absorbed

Fig. 5. PVS·⁻ formation as a function of light adsorbed, monitored by the increase in absorbance at $\lambda = 602$ nm ($\varepsilon = 12\ 500$ M⁻¹ cm⁻¹). (a) Ru(bipy)₃²⁺ as sensitizer; curve a, SiO_2 system; curve b, homogeneous system; curve c, micellar system; curve d, NaLS micellar system with 0.1 M NaCl. (b) Zn-TMPyP⁴⁺ and Zn-TPPS⁴⁻ as sensitizers: curve a, SiO_2 system with Zn-TMPyP⁴⁺; curve b, homogeneous system with ZnOTMPyP⁴⁺; curve c, SiO_2 system with Zn-TPPS⁴⁻; curve d, homogeneous system with ZnOTPPS⁴⁻.
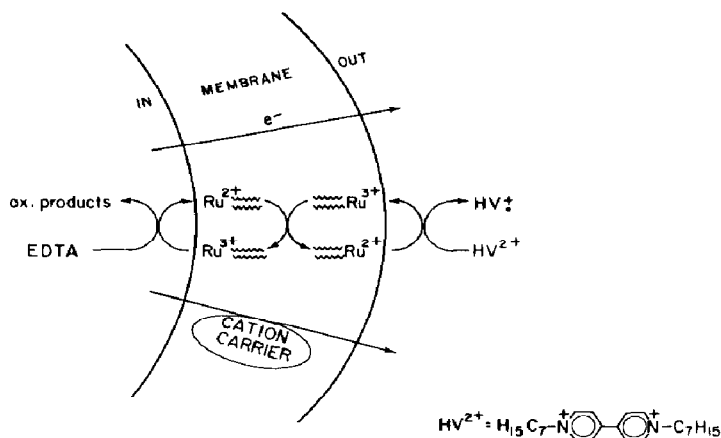
Fig. 6. Schematic function of SiO_2 particles in separating photoproducts.

is repelled. Consequently, the electrostatic interactions introduce a barrier to the degradative geminate recombination of the photoproducts. As a result, the further effective utilization of the oxidized product $Ru(bipy)_3^{3+}$ in oxidizing the electron donor TEA is facilitated and high quantum yields are obtained.

The function of the SiO_2 colloid in retarding back-electron transfer reactions has been confirmed by several methods.

(a) The quantum yield in the SiO_2 colloid depends strongly on the ionic strength of the medium. By increasing the ionic strength the interfacial surface potential is decreased. As a result, the electrostatic interactions with the interface are reduced and the quantum yield is decreased.

(b) Substitution of the positive sensitizer with one that is negatively charged yields two photoproducts that are repelled by the interface. Thus, the function of the interface in separating the active intermediates is lost. Indeed, with a negatively charged sensitizer zinc *meso*-tetraphenylporphyrin sulfonate ($Zn-TPPS^{4-}$ 4) there is no enhancement of quantum yield in the SiO_2 system (Fig. 5(b)).

(c) The back-electron transfer reaction of the intermediate photoproducts (eqns. (3) and (4)) was directly followed in the SiO_2 colloid by means of flash photolysis and was compared with the similar process in a homogeneous phase. A significant retardation of back-electron transfer was observed. With $Zn-TMPyP^{4+}$ as sensitizer, the recombination rate constant (eqn. (3)) in the SiO_2 colloid is reduced by a factor of 100 relative to the value in a homogeneous phase. Similarly, with $Ru(bipy)_3^{2+}$ as sensitizer the recombination rate is retarded about ninetyfold in the SiO_2 colloid.

The extent to which back-electron transfer reactions are retarded in the SiO_2 colloid can be improved by introduction of multinegatively charged electron acceptors such as $Fe(CN)_6^{3-}$ that increase the repulsive interactions with the interface [16]. However, with such electron acceptors the primary electron transfer event is expected to be rather inefficient because they cannot approach the interface. In order to keep the balance of efficient quenching of the excited state together with a substantial retardation of the recombination rate, two coupled

202

electron acceptors can be used. For this purpose, a colloidal SiO_2 system has been designed in which $Ru(bipy)_3^{2+}$ is the sensitizer, PVS° **5** is the primary electron acceptor and TEA the electron donor. A secondary electron acceptor, $K_3Fe(CN)_6$, is introduced into the system to provide a sink for the electron (Fig. 7). The complete photosensitized electron transfer process results in the reduction of $Fe(CN)_6^{3-}$ to $Fe(CN)_6^{4-}$ (Fig. 8). It appears that the photosensitized reaction is enhanced at least sixtyfold relative to the reaction in a homogeneous phase [16].

The sequence of events occurring in this photosensitized electron transfer has been followed by flash photolysis. The reduced primary electron acceptor
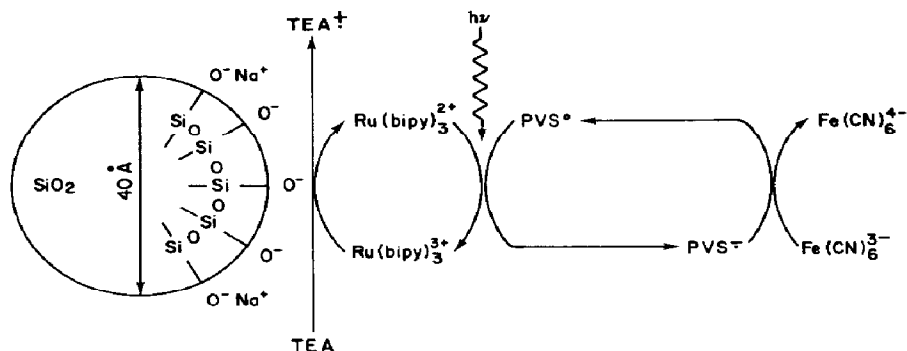
Fig. 7. Schematic function of SiO_2 particles in separating multicharged photoproducts.
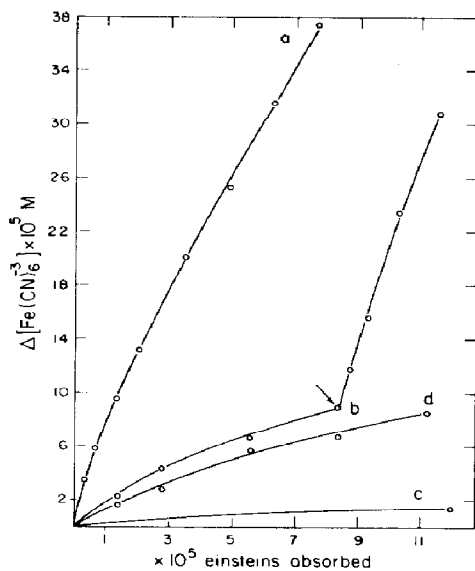
Fig. 8. The reduction of $K_3Fe(CN)_6$ as a function of light absorbed: curve a, SiO_2 system including PVS°; curve b, SiO_2 system (the arrow indicates the time of PVS° addition); curve c, homogeneous system; curve d, NaLS micellar system.

PVS$\cdot^-$ is produced by the quenching of the excited sensitizer adsorbed to the SiO_2 interface (eqn. (4)). The reduced species is ejected into the continuous aqueous phase where $Fe(CN)_6^{3-}$ is reduced in a "dark" reaction:

$$PVS\cdot^- + Fe(CN)_6^{3-} \rightarrow PVS^\circ + Fe(CN)_6^{4-} \tag{5}$$

The intermediate photoproducts thus created, $Ru(bipy)_3^{3+}$ and $Fe(CN)_6^{4-}$, tend to back-react:

$$Ru(bipy)_3^{3+} + Fe(CN)_6^{4-} \xrightarrow{\ k_b\ } Ru(bipy)_3^{2+} + Fe(CN)_6^{3-} \tag{6}$$

In a homogeneous system this process is diffusion controlled ($k_b \approx 10^{10}\ M^{-1}\ s^{-1}$) [17]. However, in the SiO_2 colloid a substantial inhibition of the recombination rate is observed ($k_v = 10^6 - 10^7\ M^{-1}\ s^{-1}$). These results indicate that the different functions required for an efficient electron transfer process can be achieved by coupling two or more electron acceptors.

4. Correlation of quantum yields with interfacial potentials

The function of the SiO_2 colloid in the photosensitized electron transfer originates from selective interactions of the components with the interface. The electrical properties of the interface and the binding characteristics of the positively charged sensitizer $Ru(bipy)_3^{2+}$ have been examined by means of flow dialysis ($K_{ass} = 1.1 \times 10^2\ M^{-1}$) [18]. The number of binding sites on each SiO_2 particle has been determined to be 65. These ionic sites establish an interfacial surface potential of about -170 mV.

The quantum yield for the photosensitized reduction of PVS° (using $Ru(bipy)_3^{2+}$ as sensitizer) has been correlated with the interfacial surface potential of the SiO_2 colloid (controlled by varying the ionic strength of the medium) [18]. The correlation curve (Fig. 9) shows that up to an interfacial potential of about -40 mV the quantum yield is not affected. Increasing the potential above this apparent threshold value results in a sharp increase in the quantum yield. A similar correlation curve was obtained when Zn-TMPyP^{4+} was used as sensitizer instead of $Ru(bipy)_3^{2+}$.

The organization of components in the SiO_2 colloids and the electrostatic interactions could, in principle, be designed with other negatively charged interfaces such as micelles. The photosensitized reduction of PVS° using $Ru(bipy)_3^{2+}$ as sensitizer and TEA as electron donor has been investigated in the presence of negatively charged sodium lauryl sulfate (NaLS) micelles and has been compared with the results for the SiO_2 colloid (Fig. 5(a)) [18]. The size of the NaLS micelles is similar to that of the SiO_2 particles. The sensitizer $Ru(bipy)_3^{2+}$ appears to bind firmly to the micellar interface ($K_{ass} = 3.5 \times 10^3\ M^{-1}$). Yet, the quantum yield for the PVS$\cdot^-$ formation is fourfold less efficient than that observed in the SiO_2 colloid. This result is attributed to the difference in the surface potential of the two interfaces. Flow dialysis measurements [18] indicate that the NaLS micellar interface has a surface potential of only -85 mV, significantly lower than the value determined for the SiO_2 interface (-170 mV).
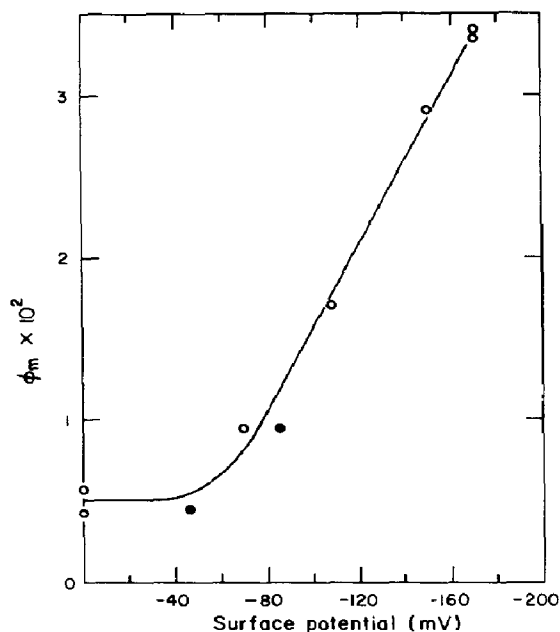
204

Fig. 9. The quantum yield for PVS·⁻ formation as a function of the surface potential of negatively charged interfaces: O, SiO_2 system; ●, NaLS micellar system.

The experimental quantum yields in the NaLS micellar system fit nicely into the correlation curve shown in Fig. 9. This indicates that because of the relatively low surface potential of the micelles the electrostatic interactions are not as effective. A comparison of the photoinduced reaction in the SiO_2 colloid with that occurring in the NaLS micelles implies that both interfaces are capable of exerting electrostatic interactions. This can be used for organizing the components involved in the photochemical reaction. However, the physical characteristic of the electric field of the different interfaces is rather important in controlling the reaction. In the NaLS micellar system, despite the organization of the components, the surface potential is relatively low and limits the ability to retard back reaction.

5. Chemical utilization of the photoproducts in the photodecomposition of water

The different interfacial systems described here represent supramolecular assemblies for the separation and stabilization of photoproducts. These photoproducts generated in the electron transfer reactions are an oxidized sensitizer and a reduced species (acceptor). In all systems that have been described here a sacrificial electron donor (EDTA or TEA) has been used. For any practical configuration, this sacrificial component must be excluded and water itself should be the compound oxidized. The oxidized intermediates ($Ru(bipy)_3^{3+}$ and Zn-TMPyP^{5+}) have the potential for oxidizing water to oxygen ($E_0(Ru(bipy)_3^{3+}/$
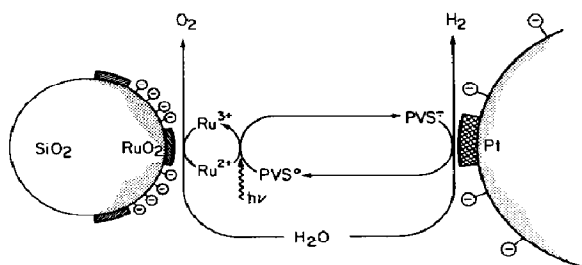
Fig. 10. The utilization of SiO_2 particles in the photodecomposition of water.

$Ru(bipy)_3{}^{2+}) = 1.26$ V; $E_0(Zn\text{-}TMPyP^{5+}/Zn\text{-}TMPyP^{4+}) = 1.2$ V) but, since the reaction requires a concerted four-electron process while the photoproducts are single-electron oxidants, a mediating charge storage catalyst is needed. In recent years transition metal oxides and, in particular, RuO_2 and PtO_2 have been reported to act as oxygen evolution catalysts with $Ru(bipy)_3{}^{3+}$ as oxidant [19, 20]. In an analogous way, the reduced species produced in the photosensitized reaction should be coupled to hydrogen evolution. Reduced bipyridinium salts (viologen radicals) are capable of reducing water to hydrogen [21, 22]. For this reaction colloidal platinum has been found to be an efficient charge storage catalyst.

A schematic view of one possible complete system is shown in Fig. 10. Since the oxidized photoproduct, e.g. $Ru(bipy)_3{}^{3+}$, is associated with one colloidal particle, its interface should be coated with an oxygen-evolving catalyst. An additional colloidal site is introduced by supporting platinum on a negatively charged polymer. The electrostatic repulsions of the two negatively charged interfaces would prevent agglomeration. By using a polymer with a low enough surface potential the approach of the reduced photoproduct PVS·⁻ to the hydrogen evolution catalyst would be permitted while its recombination with $Ru(bipy)_3{}^{3+}$ on the other, more highly charged, colloid would be prevented. In this way, the vectorial character of the electron transfer process could be used for an efficient cleavage of water.

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