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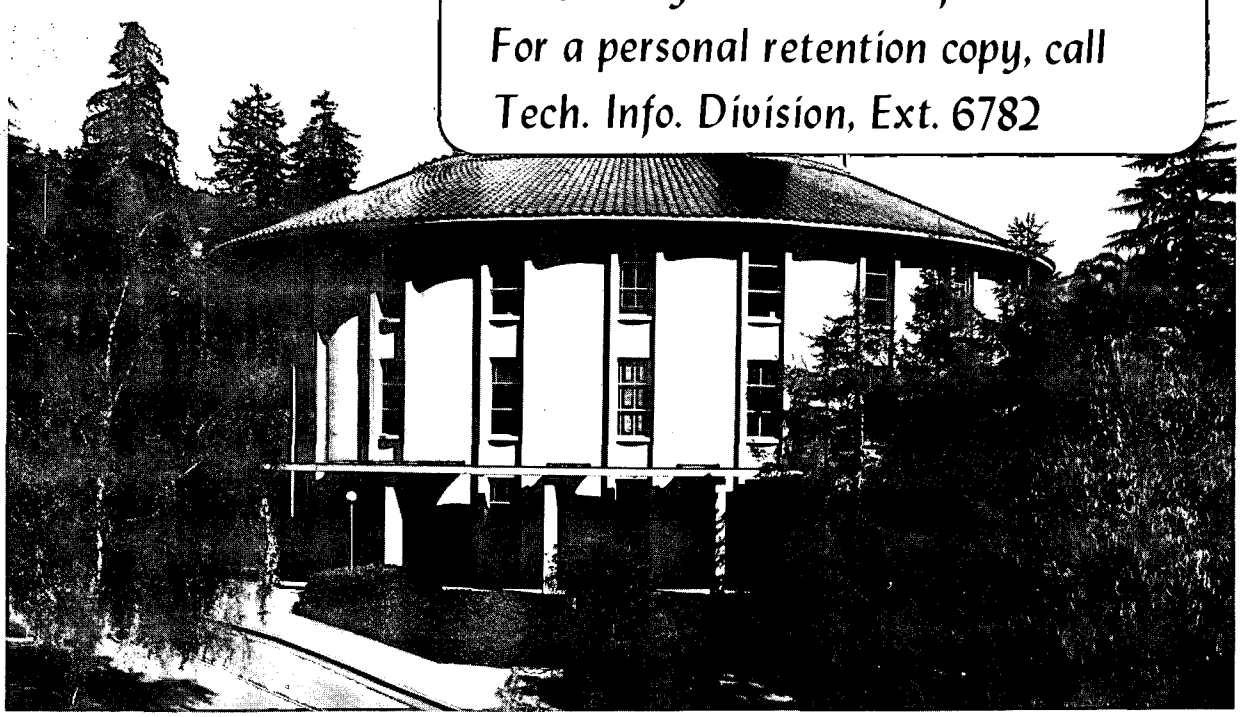

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PHOTOSENSITIZED ELECTRON TRANSFER PROCESSES IN SiO_2 COLLOIDS AND NaLS MICELLAR SYSTEMS: CORRELATION OF QUANTUM YIELDS WITH INTERFACIAL SURFACE POTENTIALS

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Abstract

The photosensitized reduction of propylviologen sulfonate, PVS^o, has been investigated in a SiO_2 colloidal system and compared to the homogeneous aqueous phase and/NaLS micellar system. In these systems, $Ru(bipy)_3^{2+}$ is used as sensitizer and triethanolamine, TEA, is the ultimate electron donor. The quantum yield for $PVS^{\bar{\cdot}}$ formation in the SiO_2 colloid ($\emptyset = 3.3 \times 10^{-2}$) is 6.6-fold higher than the value obtained in the homogeneous system ($\emptyset = 5 \times 10^{-3}$). Similarly, the quantum yield for $PVS^{\bar{\cdot}}$ production in SiO_2 systems is ca. 4-fold more efficient than the value obtained in the NaLS micellar solution ($\emptyset = 8.6 \times 10^{-3}$). The high quantum yields obtained in the SiO_2 colloidal system are attributed to stabilization against back reaction of the intermediate photoproducts, i.e., $Ru(bipy)_3^{3+}$ and $PVS^{\bar{\cdot}}$, by means of electrostatic repulsion of the reduced electron acceptor from the negatively charged particle.

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The binding properties of the SiO_2 particles have been investigated by the flow dialysis technique. The photosensitizer, $Ru(bipy)_3^{2+}$, is firmly associated with the colloidal particles ($K_{ass.} = 1.1 \times 10^2\ M^{-1}$), and the number of ionized sites on the particle is 65. From the Gouy-Chapman theory, the surface potential of the particles has been estimated at different ionic strengths and correlated with the quantum yields of the photosensitized electron transfer process. The correlation curve reveals that an interfacial surface potential up to ca.-40 mV does not affect the quantum yield. However, increasing the surface potential over this value rapidly increases the quantum yields. The micellar NaLS system has been similarly characterized by flow dialysis.

While the sensitizer $Ru(bipy)_3^{2+}$ associates strongly with the NaLS micelle ($K_{ass.} = 3.5 \times 10^3\ M^{-1}$), the micellar interface is characterized by a significantly lower surface potential (ca. -85 mV vs. -170 mV). The quantum yield obtained in the micellar system at different ionic strengths fits nicely on the correlation curve for the colloidal SiO_2 system.

INTRODUCTION

The development of devices that convert solar energy into chemical energy is currently of great interest[1]. One approach involves mimicing natural photosynthesis to the extent that water is decomposed to hydrogen and oxygen[2,3]. The idea is to photosensitize an electron transfer process whereby a reduced electron acceptor and an oxidized electron donor are formed (eq.1). Coupling of these intermediate photoproducts to the decomposition of water should form a cyclic device that converts water into a potential fuel (hydrogen). In the past few years significant progress in the development of such devices has been made. Particular attention has been devoted to the photosensitized reduction of 4,4'-bipyridinium salts (viologens) by synthetic sensitizers such as $Ru(bipy)_3^{2+}$ and Zn-porphyrins[4-6]. With these systems the reduction of water to hydrogen as well as the photo-oxidation of water to oxygen with the aid of heterogeneous catalysts, e.g., Pt, PtO_2 and RuO_2, has been achieved[7-10].

$$D + A \underset{k_b}{\overset{h\nu}{\rightleftharpoons}} D^+ + A^- \qquad \text{(eq.1)}$$

However, one fundamental limitation of such systems is the energetically favored back reaction of the initially formed photoproducts. Thus, to facilitate the subsequent utilization of the photoproducts the back electron transfer should be retarded. Several approaches such as functionalized micelles[11-14], liposomes[15-17], microemulsions[18,19] and polyelectrolytes[20,21] have been used as a means for stabilizing charge separation. In these systems the electrostatic interactions of the photoproducts with charged interfaces play a key role.

Recently we have investigated the use of a colloidal SiO_2 solid interface for such a purpose[22]. Here, we wish to compare the effects of the solid negatively charged SiO_2 interface to those of the negatively charged NaLS micellar interface on the electron transfer process. Furthermore, the physical characterization of the colloidal system allows one to correlate the photosensitized electron transfer characteristics with interfacial properties.

EXPERIMENTAL SECTION

Materials. N,N'-dipropyl-4,4'-bipyridinium sulfonate (PVS^o) was prepared as described recently[23]. The system was prepared by diluting a commercial 14.5% SiO_2 40 Å suspension (Nalco) to 0.2% and adjusting the pH to 9.8 with 0.1 M HCl. The electron acceptor, PVS^o (1×10^{-3} M), $Ru(bipy)_3^{2+}$ (6×10^{-5} M) and triethanolamine (1×10^{-3} M) are added to the colloidal SiO_2 suspension. In the micellar systems, SiO_2 was substituted by sodium lauryl sulfate, NaLS (1.5×10^{-2} M). The micellar solutions and the homogeneous aqueous systems were adjusted to pH 9.8. The investigated solution (3 ml) was transferred to a 1 x 1 cm glass cuvette equipped with a teflon stirring bar, a valve and serum stopper. The system was deaerated by repeated evacuation of argon flushing

Illumination. The cuvette was immersed in a water bath (23 ± 2°C) made of a plexiglass box with a 2 x 1 cm window, and the solution in the cuvette was stirred magnetically during illumination. The light source was a 1000-W xenon arc lamp (Oriel Universal Arc Lamp Source, Model C-60-50) whose beam was filtered to give blue light (440-550 nm) through a cupric sulfate solution and two glass filters (Corning 3-72

and 5-57). The incident photon flux was $2.7 \pm 0.4 \times 10^{-7}$ einstein·sec^{-1}·cm^{-2} as determined by Reinecke salt actinometry[24]. The production of propylviologen sulfonate radical anion, $PVS^{\overline{\cdot}}$, was monitored by following its absorbance at 602 nm or 735 nm. Extinction coefficients of the radical absorption were determined chemically using dithionite reduction[25]. The extinction coefficients are $\varepsilon(602\ nm) = 12.800\ M^{-1}\cdot cm^{-1}$ and $\varepsilon(735) = 3200\ M^{-1}\cdot cm^{-1}$. The quantum yield (Ø) was calculated by dividing the maximal rate of $PVS^{\overline{\cdot}}$ formation by the rate of quanta absorbed.

Binding Studies. Binding studies were performed with the flow dialysis technique. The apparatus and analytical method have been described previously[26]. The upper and lower chambers were separated by standard cellulose dialysis tubing (VWR Scientific, M.W. cut-off 6,000-8,000). Both chambers are well stirred by means of small magnetic stirring bars. The upper chamber (0.5 ml) contained the same solution (water,pH 10.2) as was pumped through the lower chamber at a rate of 1 ml/min (LKB pump,Model 2000). At time zero either $Ru(bipy)_3^{2+}$, methyl red or PVS^o (see text) were added to the upper chamber up to a final concentration of 8×10^{-3} M. Fractions of 1.0 ml from the lower chamber were collected at 1 minute intervals and assayed spectroscopically. In the case of $Ru(bipy)_3^{2+}$ and methyl red the absorbance $\lambda = 460$ nm was monitored and for PVS^o the absorbance at $\lambda = 265$ nm.

After a steady state had been reached between the two chambers of the system, SiO_2 particles were added to the upper compartment and further fractions collected from the lower chamber were analyzed. Dodecyltrimethylammonium chloride (2×10^{-2} M) was added to the upper chamber at the time indicated (see text). Further dialyzed fractions were collected at 1 minute time intervals.Binding studies to micelles were similarly investigated by the

flow dialysis technique. In these experiments micelles were added at t = 0 together with $Ru(bipy)_3^{2+}$ and the system dialyzed until a steady state had been reached between the two chambers. The micellar equilibrated system is compared to the homogeneous dialyzing curve in order to deduce the binding properties. The fraction of $Ru(bipy)_3^{2+}$ bound to the negatively charged interfaces was calculated according to Ramos et al.[27]. (Further details will be given in the text.)

RESULTS AND DISCUSSION

Photosensitized Reduction of PVS^o in SiO_2 Colloidal Systems.

The SiO_2 colloids employed in our study are composed of particles with a mean diameter of 40 Å. At pH > 6 the silanol groups on the particle surface are ionized, and an electrical double layer is produced[28,29]. Consequently, the particles repel each other and their agglomeration is prevented. The solid particle is characterized by a high (negative) surface potential which results in the attraction of positively charged species[30]. In particular, it seemed feasible to us that the SiO_2 solid interface should be capable of producing electrostatic attractions and repulsions with charged species formed in photosensitized electron transfer processes[22]. Thus, the separation of the oppositely charged photoproducts, and retardation of back electron transfer reactions, by means of these coulombic interactions seemed achievable.

Illumination of the colloidal SiO_2 suspension that includes $Ru(bipy)_3^{2+}$ as sensitizer, propylviologen sulfonate, PVS^o, 1, as electron acceptor and triethanolamine, TEA, as electron donor results in the production of propylviologen sulfonate radical ($PVS^{\cdot -}$). Its rate of formation is depicted in Fig. 1a. The quantum yield for $PVS^{\cdot -}$ formation

appears to be $\emptyset = 3.3 \times 10^{-2}$. Exclusion of the SiO_2 particles and performing the similar experiment in a homogeneous aqueous phase results in a significantly lower quantum yield for $PVS^{\bar{\cdot}}$ formation (Fig. 1b), $\emptyset = 5 \times 10^{-3}$. The enhancement of the quantum yield of $PVS^{\bar{\cdot}}$ production is rationalized by electrostatic interactions introduced by the negatively charged SiO_2 solid interface which retard back electron transfer of the photoproducts (Fig. 2). The positively charged sensitizer ($Ru(bipy)_3^{2+}$) is bound to the negatively charged interface(vide infra). Excitation of the sensitizer followed by its quenching by the electron acceptor (PVS^o) <u>via</u> an electron transfer mechanism results in the formation of the oxidized sensitizer and the reduced electron acceptor, $PVS^{\bar{\cdot}}$. The negatively charged interface assists the separation of the ion pair and ejects the $PVS^{\bar{\cdot}}$ into the continuous aqueous phase, while the oxidized sensitizer remains attached to the negatively charged particle. Due to electrostatic repulsions between the negatively charged interface and the reduced electron acceptor, the recombination of the photoproducts is hindered and, therefore, the back electron transfer is retarded (eq.2). The subsequent oxidation of triethanolamine by the intermediate oxidized sensitizer completes the cycle. The amount of $PVS^{\bar{\cdot}}$ formed after 3×10^{-5} einsteins are absorbed (2.2×10^{-4} M) relative to the initial sensitizer concentration indicates that the sensitizer is recycled during the electron transfer process. Introduction of air into the system re-oxidizes $PVS^{\bar{\cdot}}$ and the amount of sensitizer determined by its absorbance at $\lambda = 460$ nm appears to be unchanged relative to its initial concentration.

The function of the SiO_2 interface in retarding the back electron transfer reaction of the intermediate photoproducts has been confirmed by a flash photolytic study of the system (Fig. 3)[31]. In the homogeneous system the photoproducts decay rapidly (eq.2) with a bimolecular rate constant close to that of a diffusion controlled process ($k_b = 3.6 \times 10^9\ M^{-1} \cdot sec^{-1}$). In the SiO_2 colloidal system a substantial decrease (24-fold) in the recombination rate is observed ($k_b = 1.5 \times 10^8\ M^{-1} \cdot sec^{-1}$). Thus, the enhanced quantum yield of the photosensitized process is confirmed to be the inhibition of back reactions.

$$Ru(bipy)_3^{3+} + PVS^{\cdot -} \longrightarrow Ru(bipy)_3^{2+} + PVS^{o} \quad \text{(eq.2)}$$

The surface potential of the SiO_2 particles depends on the ionic strength of the system[32]. By increasing the ionic strength the surface potential is diminished with a consequent reduction in the quantum yield. Indeed, it can be seen (Fig. 4) that the quantum yield of the electron transfer process strongly depends on the ionic strength of the system. At an ionic strength of 0.5 M NaCl the quantum yield declines to a value of $\emptyset = 9.0 \times 10^{-3}$, a 6-fold decrease relative to the value without added salt. Furthermore, it can be noted that this value approaches the quantum yield obtained in the homogeneous system.

The effect of salt on the surface potential of such charged particles is predicted by the Gouy-Chapman relation (with Stern modification[32,33]) (eq.3)

$$\sigma_s = \left(\frac{2\ DRT}{\pi}\right)^{1/2} (C)^{1/2} \sinh\left(\frac{F\Psi_\delta}{2RT}\right) \quad \text{(eq.3)}$$

where σ_s is the surface charge density of the particle; Ψ_δ, the surface potential; D, the dielectric constant; R, the universal gas constant; F, the Faraday constant; T, the absolute temperature and C, the concentration of electrolyte. The number of ionized

sites on a 40 Å SiO_2 particle has been determined[30] to be ∿ 60. (This value is confirmed independently in our work (vide infra.) Thus, the charge density is ∿ 0.18 C/m^2, which corresponds to a surface potential at a salt concentration of 0.01 M of ∿ -170 mV. Addition of extra salt and increasing the ionic strength results in the reduction of the surface potential. At 0.1 M NaCl the surface potential drops to -108 mV and at 0.5 M NaCl the surface potential is decreased to -72 mV. The experimental quantum yield of the photosensitized electron transfer process as a function of the surface potential of the charged particles is shown in Fig. 5. It can be seen that the quantum yield is almost unaffected up to a surface potential of ca. -40 mV. Increase of the surface potential above this apparent threshold value results in a rapid increase in the quantum yield. This dependence of the electron transfer quantum yield on the particle surface potential is expected in view of our previous discussion. By decreasing the surface potential at the interface, the coulombic interactions leading to the separation of the photoproducts are decreased. Consequently, the back electron transfer reactions (eq.2) are enhanced, and the effectiveness of the interface is reduced. The flash photolysis in the presence of added salt[31] confirms this explanation. The decay rate of the intermediate photoproduct in the SiO_2 colloids in the presence of added salt (0.1 M NaCl) is enhanced significantly ($k_b = 4 \times 10^8\ M^{-1} \cdot sec^{-1}$) relative to the system with no added salts.

Photosensitized Reduction of PVS^o in NaLS Micelles.

Micelles have been widely explored in the past as potential interfaces for retarding back electron transfer by coulombic interactions[11-16]. Micellar aggregates are close in their size (ca. 40 Å diameter)[11b,34] to the solid SiO_2 particles. Thus, it was interesting to compare and relate the effectiveness of the SiO_2 particles to that of a negatively charged micellar surface. The previously described system including $Ru(bipy)_3^{2+}$ as sensitizer, PVS^o as electron acceptor and TEA as electron donor in a medium of negatively charged sodium lauryl sulfate, NaLS, micelles has been explored (CMC for NaLS micelles 8.1×10^{-3} M)[13a,34]. The rate of reduction of $PVS^{\cdot-}$ upon illumination is shown in Fig. 1c. The quantum yield for the electron transfer process is only twice the value obtained in the homogeneous system, and ca. 4-fold lower than the corresponding quantum yield in the colloidal SiO_2 system. The physical characterization of micelles, and, in particular, NaLS micelles is well documented in the literature[34]. It appears that although there is no difference in size between the micelles and the SiO_2 particles, they differ significantly in the number of ionized groups and consequently in their charge density. The aggregation number of NaLS micelles is 62, and about 1/6 (or $\sim$ 17%) of these headgroups are in an ionized form. Thus, the number of ionized sites on an NaLS micelle is ca. 10 and corresponds to a charge density of approximately $\sigma_s = 0.04\ C/m^2$. Using (eq.3) the NaLS micelle is characterized by a surface potential of $\sim$ -90 mV. The quantum yield obtained in the micellar NaLS system fits nicely on the curve of quantum yields vs. surface potential as derived for the SiO_2 system (Fig. 5). As in the colloidal SiO_2 system, the surface potential of micelles is reduced by increasing the ionic strength. Addition of salt

to the micellar NaLS system ([NaCl] = 0.1 M) reduced the quantum yield of the photosensitized electron transfer to a value of $\emptyset = 5 \times 10^{-3}$ (Fig. 1d). At this ionic strength the calculated micellar surface potential is -44 mV. Despite this fact, the quantum yield of the electron transfer process is identical to that obtained in the homogeneous system and is in agreement with the curve formulated for the SiO_2 system (Fig. 5).

These results clearly demonstrate a relation between the interfacial surface potential leading to the separation of the photoproducts and the quantum yield of the photosensitized electron transfer process. Although at present we are not able to explain the shape of this curve, several points should be emphasized. The design of interfaces with even higher charge densities is expected to improve the quantum yields. Furthermore, common micellar aggregates are usually characterized by a low surface potential[34] and thus are limited in their capability to improve quantum yields. However, modifications of the micellar structure (for example, by introducing heavy metals as counter ions) might improve the charge density and consequently increase their function in enhancing the quantum yields[12a,34].

Binding of $Ru(bipy)_3^{2+}$ to the SiO_2 and NaLS Charged Interfaces.

Positively charged species are known to bind to SiO_2 and negatively charged micelles[30,35]. Several methods for characterization of the binding of positively charged molecules to SiO_2 particles have been used, including spectroscopic titrations and radioactive labeling[30]. Similarly, the association of positively charged species to negatively charged micelles has been well characterized using X-ray diffraction, spin labeling techniques, absorption and NMR spectroscopy[36]. We have found

that flow dialysis[26,27] is a particularly simple and useful technique for characterization of the binding properties of sensitizers to silica colloids and micelles. This technique has been widely used in studying binding of low molecular weight ligands to enzymes[26,37] and uptake of permeable substrates by bacterial membranes[27,38]. The flow dialysis apparatus is composed of two compartments, separated by a dialysis membrane. Into the upper chamber, a solution of $Ru(bipy)_3^{2+}$ is introduced. $Ru(bipy)_3^{2+}$ dialyzes through the membrane into the lower chamber and by means of a flow of solution through the lower chamber fractions are collected at time intervals. A typical curve of the $Ru(bipy)_3^{2+}$ concentration in the lower chamber measured spectroscopically (λ_{max} = 460 nm) at the different time intervals is shown in Fig. 6a. It can be seen that shortly after the addition of $Ru(bipy)_3^{2+}$ to the upper chamber, $Ru(bipy)_3^{2+}$ appears in the dialysate (lower chamber), increases linearly for about 3 minutes, and reaches a maximum which then decreases at a slow rate. In the latter part of the curve, the amount of $Ru(bipy)_3^{2+}$ appearing in the dialysate is directly proportional to the concentration of free sensitizer in the upper chamber. Upon addition of the SiO_2 particles to the upper chamber, a sharp decrease of the $Ru(bipy)_3^{2+}$ in the lower chamber is observed, and a new steady state between the two chambers is established. This indicates that $Ru(bipy)_3^{2+}$ binds to the particles (Fig. 6a). Surfactants are known to bind strongly to SiO_2 particles[30]. Addition of an excess of dodecyltrimethylammonium chloride, DTMA, to the upper chamber indeed releases the $Ru(bipy)_3^{2+}$ from the particles, and consequently its concentration in the lower chamber increases and reaches the level observed in the experiment performed without added particles (Fig. 6a1). From this type of

curve the number of $Ru(bipy)_3^{2+}$ molecules bound to one particle can be derived[27]. A value of $\sim$ 65 sites per particle available for $Ru(bipy)_3^{2+}$ binding was found. Furthermore, the fraction of $Ru(bipy)_3^{2+}$ bound to the particle (α) can easily be determined for any given particle concentration and a value for the Michaelis binding constant (K) can be estimated from a Langmuir type plot (eq.4). P in this equation is the number of free sites available for binding.

$$\alpha^{-1} = 1 + \frac{1}{K_{ass}[P]} \qquad \text{(eq.4)}$$

A value of $K_{ass} = 1.1 \times 10^2 M^{-1}$ is estimated which indicates that $Ru(bipy)_3^{2+}$ binds strongly to the particle. An alternative explanation for the observed decrease of $Ru(bipy)_3^{2+}$ in the dialysate upon addition of SiO_2 particles could be that the permeability of the dialysis membrane for the $Ru(bipy)_3^{2+}$ is hindered, due to binding of the SiO_2 particles to the dialysis membrane. The fact that no decrease in the concentration of a negatively charged dye (methyl red) in the lower chamber is observed excludes such a possibility (Fig. 6b). In addition, Fig. 6b demonstrates that in contrast to positively charged dyes, a negatively charged dye does not bind to the particles. An essential feature of the scheme shown in Fig. 2 is that the oxidized acceptor will not bind to the particle and that the reduced form is repelled by the negatively charged sites on the particle. Fig. 6c clearly shows that the oxidized acceptor (PVS^o) does not bind to the particle.

Similar experiments were conducted with negatively charged NaLS micelles. $Ru(bipy)_3^{2+}$ was found to bind strongly to the micelles (K_{ass} = $3.5 \times 10^3 M^{-1}$). However, for micelles the number of sensitizer molecules bound per unit area was considerably less than for SiO_2 particles. A value of ∿10 sites per micelle available for $Ru(bipy)_3^{2+}$ binding was found, while in the similar sized SiO_2 particles a value of ∿65 was determined. The number of binding sites determined by the flow dialysis method are in good agreement with the ionic site values obtained for these interfaces by other methods (for SiO_2 ∿60 ionic sites[30] and for NaLS micelles ∿10[13a,34]).

Application to Photolysis of Water.

The overall photosensitized reaction achieved in the SiO_2 colloid and NaLS micellar system is the reduction of PVS^o by triethanolamine, TEA. The ultimate electron donor, TEA, is a sacrificial component in the system. It functions as a scavenger for the intermediate $Ru(bipy)_3^{3+}$ and results in an alternate route to the degradative back electron transfer reaction and recycles the photoactive component. To accomplish the photodecomposition of water, the TEA donor must be eliminated from the system, and water itself should be the final electron donor. The intermediate oxidized sensitizer $Ru(bipy)_3^{3+}$ is thermodynamically capable of oxidizing water (E^o $\left(Ru(bipy)_3^{3+}/Ru(bipy)_3^{2+} = 1.26 \text{ volt}^4\right)$. Indeed, oxygen evolution using this oxidizing species in the presence of solid catalysts such as RuO_2 has been accomplished[9,10]. It seems, therefore, feasible to support an oxygen evolution catalyst on the SiO_2 particles. Furthermore, viologen radicals are capable of reducing water to hydrogen in the presence of solid catalysts such as Pt or Rh[38]. Our experiments

were performed at pH 9.8. At this pH $PVS^{\cdot -}$ (E_o = -0.41 V) cannot reduce water to hydrogen. However, structural modifications of the electron acceptor[39] and/or lowering the pH of the medium might lead to hydrogen production. These aspects are currently being explored.

CONCLUSIONS

The SiO_2 colloid interface offers a powerful means for the stabilization of the photoproducts from photoinduced electron transfer reactions. Therefore much higher quantum yields can be obtained with the assistance of the colloid than in homogeneous systems.

Surface potentials correlate well with quantum yields for both silica and micellar interfaces, indicating that it is the high surface potential of the SiO_2 particles that is responsible for their unique activity. Even further stabilization of photoproducts might be achieved by designing multi-negatively charged compounds as reactants.

To reach the ultimate objective of the photodecomposition of water, the back-reaction of intermediate photoproducts must be prevented long enough for the process of hydrogen and oxygen evolution to take place. The use of high surface potentials to achieve this stabilization may be a productive course to follow.

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FIGURE LEGENDS

Fig. 1 Propylviologen radical, $PVS^{\cdot-}$, formation as a function of light adsorbed. All experiments were performed at pH 9.8. $[Ru(bipy)_3^{2+}] = 6 \times 10^{-5}$ M. $[PVS^o] = 1 \times 10^{-3}$, and $[TEA] = 1 \times 10^{-3}$ M. (a) 0.2% SiO_2 colloidal system; (b) homogeneous system; (c) NaLS micellar system $[NaLS] = 1.5 \times 10^{-2}$ M; (d) NaLS micellar system with added salt, $[NaCl] = 0.1$ M.

Fig. 2 Schematic function of SiO_2 particles in photosensitized electron transfer process.

Fig. 3 Transient absorbance changes of $PVS^{\cdot-}$ followed at 602 nm. Experiments were performed at pH 9.8. $[Ru(bipy)_3^{2+}] = 6 \times 10^{-5}$ M, $[PVS^o] = 1 \times 10^{-3}$ M. (a) honogeneous system; (b) 0.2% SiO_2 colloidal system.

Fig. 4 Propylviologen radical, $PVS^{\cdot-}$, formation as a function of ionic strength in the SiO_2 colloid. Experiments at pH 9.8. $[Ru(bipy)_3^{2+}] = 6 \times 10^{-5}$ M, $[PVS^o] = 1 \times 10^{-3}$, $[TEA] = 1 \times 10^{-3}$ M and 0.2% SiO_2. (a) No added NaCl; (b) $[NaCl] = 0.01$ M; (c) $[NaCl] = 0.1$ M; (d) $[NaCl] = 0.5$ M.

Fig. 5 Quantum yield for propylviologen radical, $PVS^{\cdot-}$, formation as a function of the surface potential of negatively charged interfaces. (○), SiO_2 colloid; (●), NaLS micellar system.

Fig. 6. Association of $Ru(bipy)_3^{2+}$, methyl red and PVS^o with SiO_2 particles as determined by flow dialysis. Experiments were performed at pH 9.8 as described in the experimental section. The concentration of $Ru(bipy)_3^{2+}$, methyl red and PVS^o added to the upper chamber was 8×10^{-3} M. SiO_2 was added at the time

indicated. In Fig. 6a, (1) 0%, (2) 0.03%, (3) 0.24%, (4) 0.75% of SiO_2. In Fig. 6b and 6c the concentration of SiO_2 was 0.75%. [DTMA]= 2×10^{-2} M. (a) $Ru(bipy)_3^{2+}$; (b) methyl red; (c) PVS^o.

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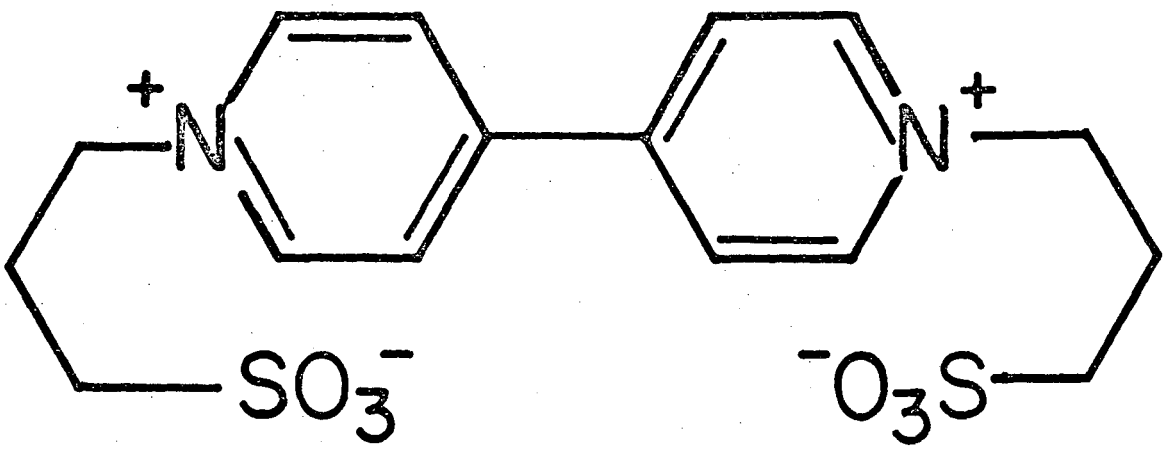

XBL 8012-2658

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(1)

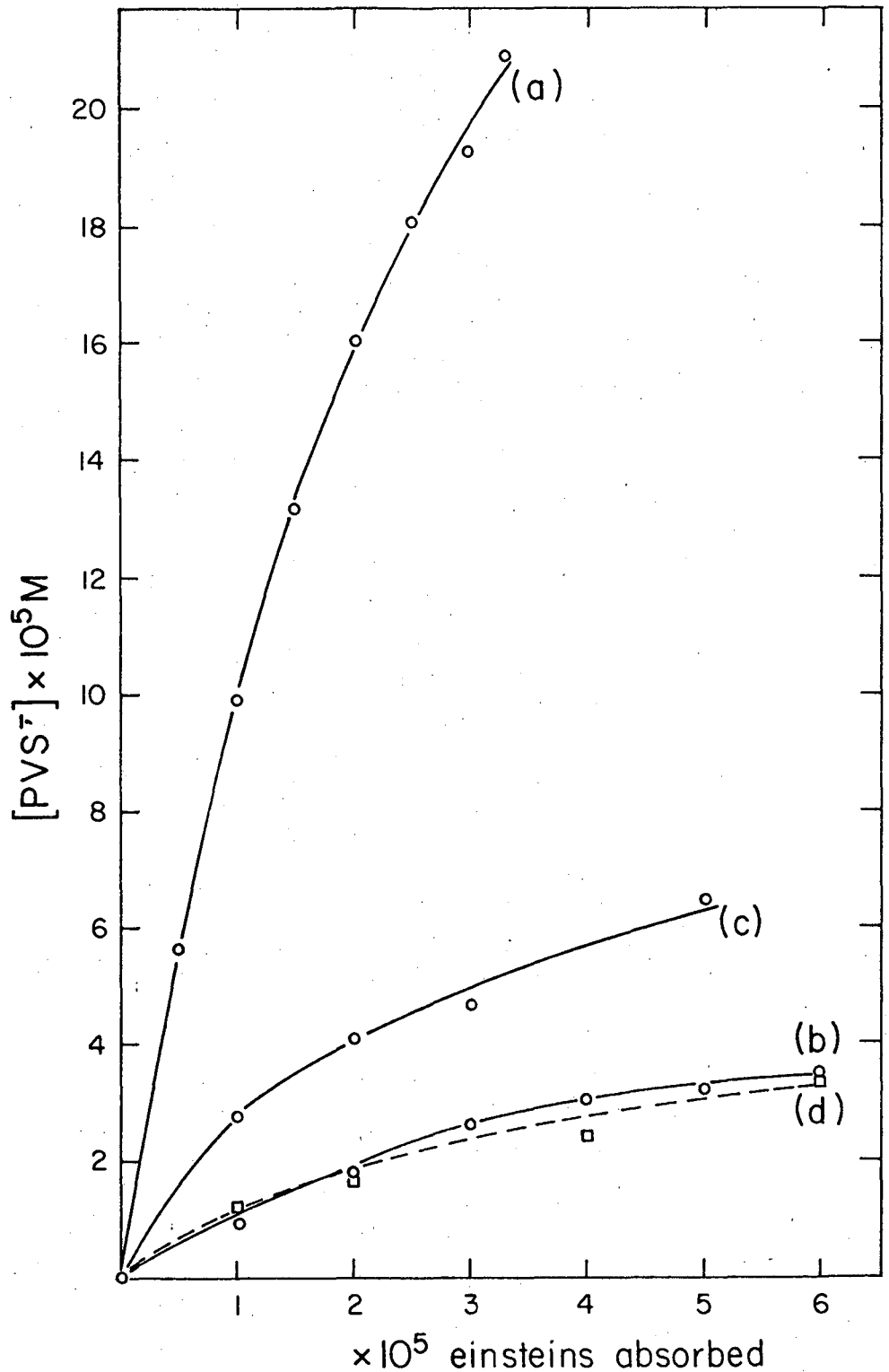

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FIGURE 1

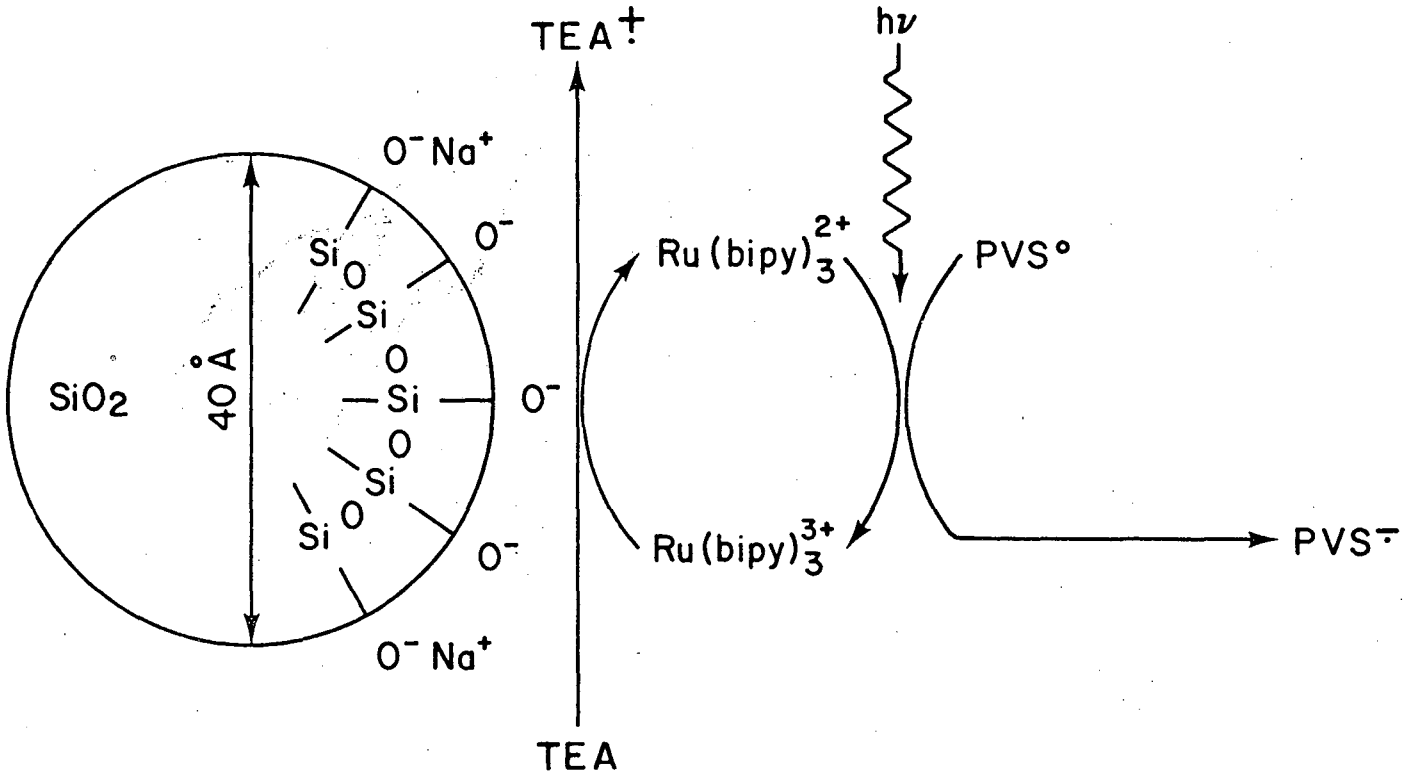

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FIGURE 2

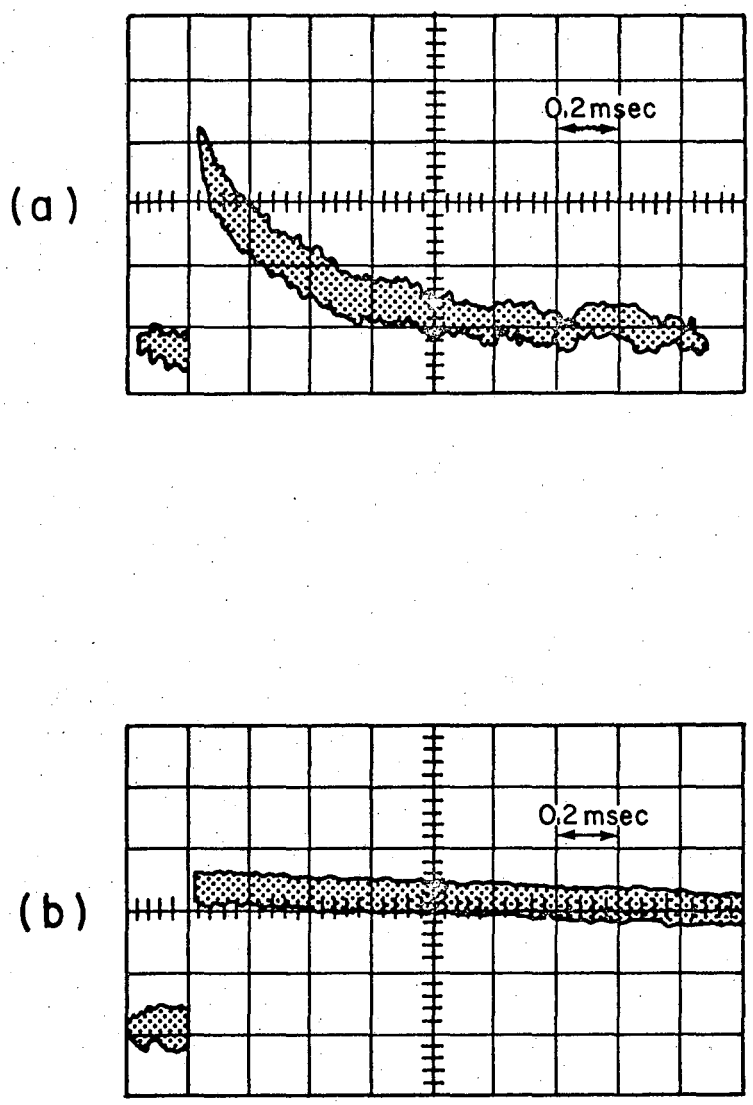

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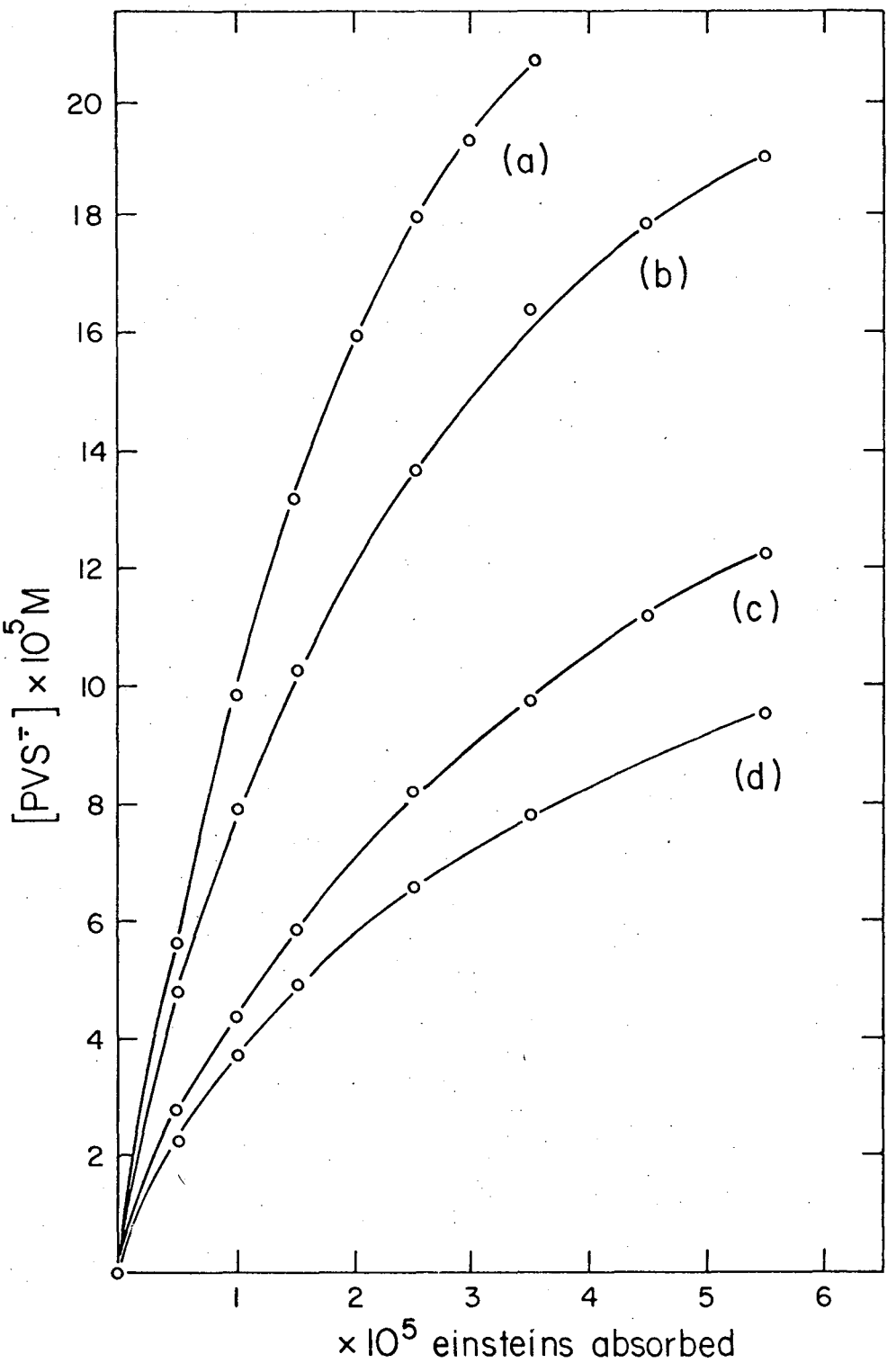
FIGURE 3



XBL 811-4423

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FIGURE 4

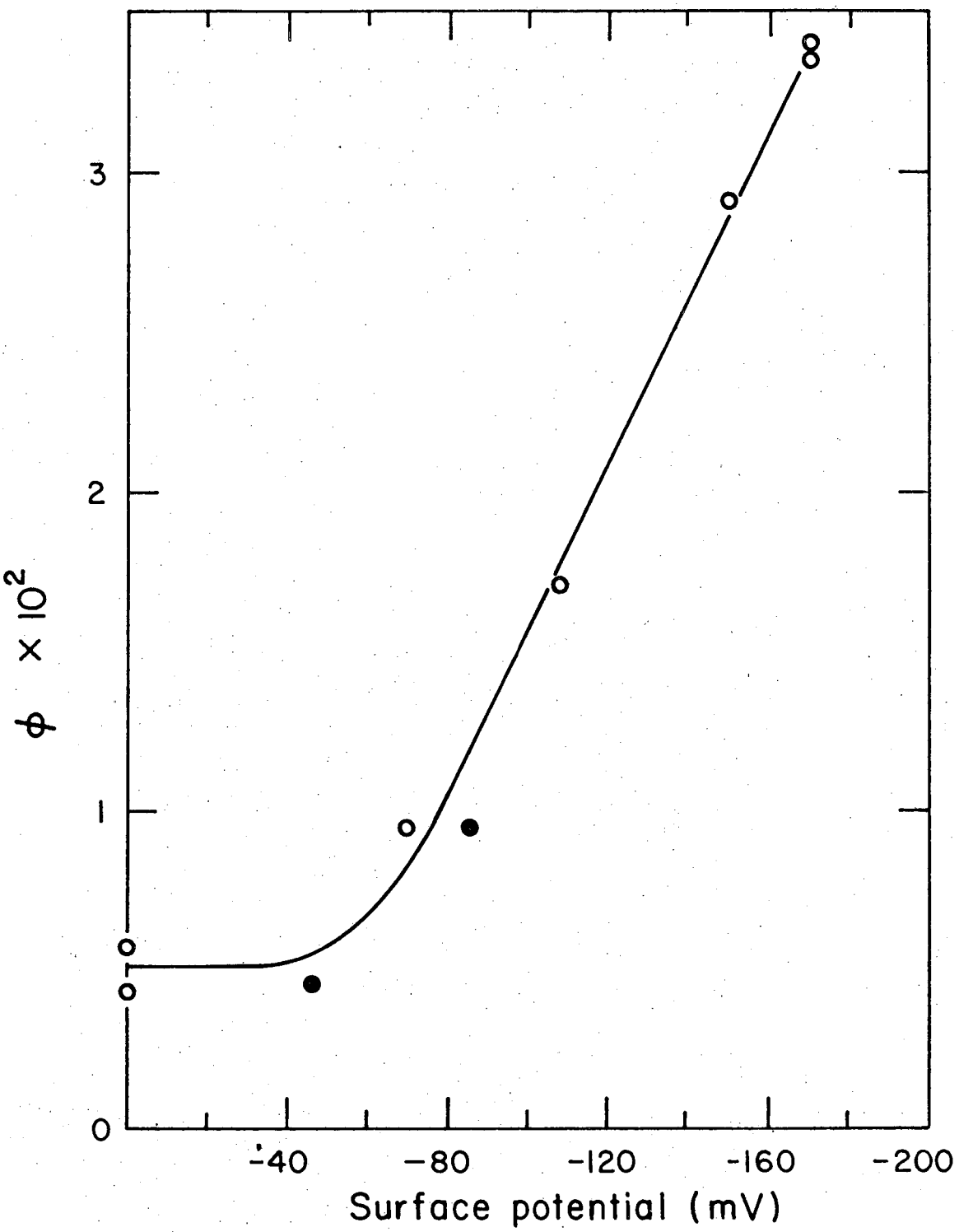

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FIGURE 5

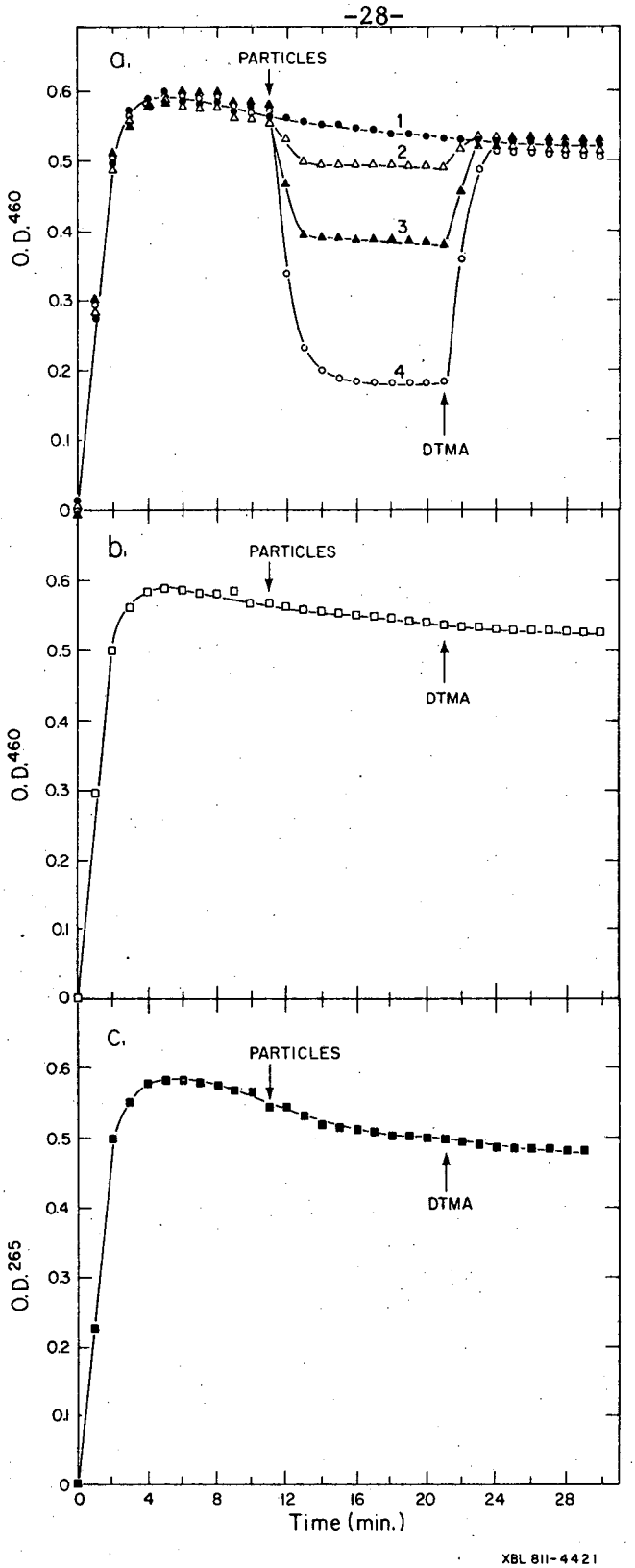

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FIGURE 6

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