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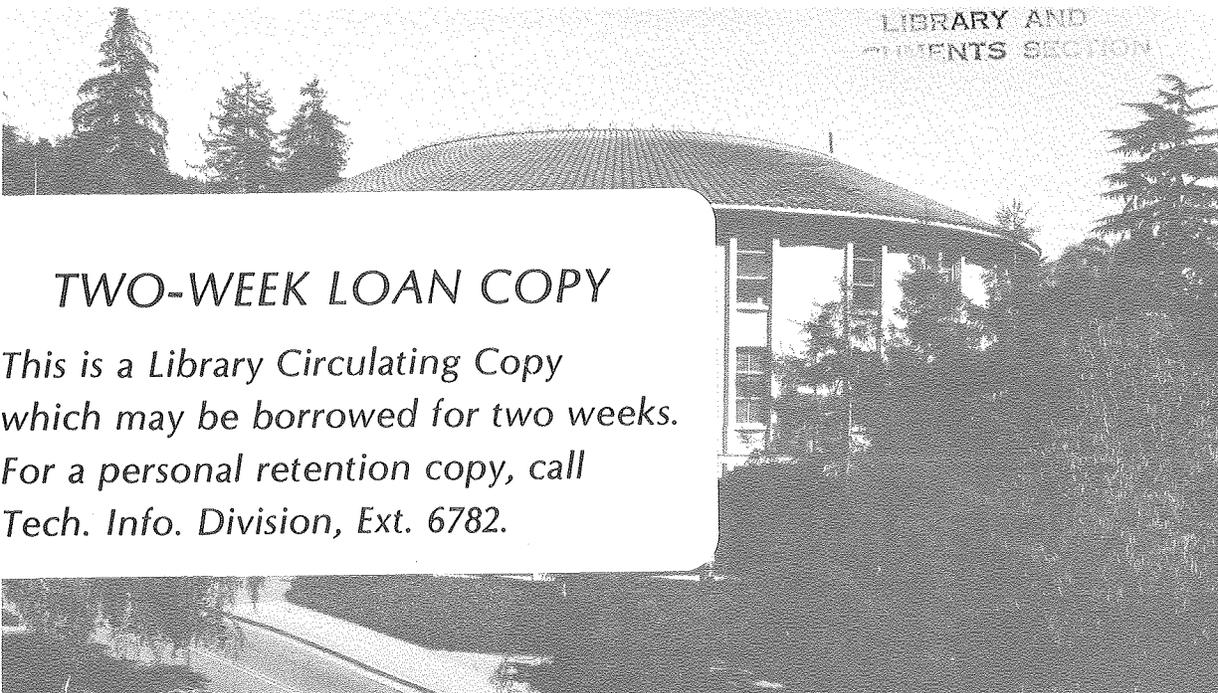
PHOTOSENSITIZED ELECTRON TRANSFER REACTIONS IN COLLOIDAL SiO_2 SYSTEMS: CHARGE SEPARATION AT A SOLID-AQUEOUS INTERFACE

Itamar Willner, John W. Otvos, and Melvin Calvin

January 1981

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PHOTOSENSITIZED ELECTRON TRANSFER REACTIONS IN COLLOIDAL SiO_2 SYSTEMS:
CHARGE SEPARATION AT A SOLID-AQUEOUS INTERFACE

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ABSTRACT

Colloidal SiO_2 particles provide an efficient solid-liquid interface that retards back-electron transfer of photochemically produced products. Consequently, high quantum yields in photosensitized electron transfer processes are obtained. The photosensitized reduction of propylviologen sulfonate (PVS^{\ominus}) by Zn-meso-tetramethylpyridinium porphyrin (Zn-TMPyP^{4+}) and $\text{Ru}(\text{bipy})_3^{2+}$, using triethanolamine as electron donor, has been investigated in the colloidal SiO_2 system and compared to the corresponding homogeneous system. Using Zn-TMPyP^{4+} as sensitizer, the quantum yield for PVS^{\ominus} production, in the SiO_2 system ($\phi_{\text{max}} = 0.37$), is 10-fold more efficient than the respective process in the homogeneous aqueous solution ($\phi_{\text{max}} = 0.038$). Similarly, when $\text{Ru}(\text{bipy})_3^{2+}$ is used as a sensitizer a 13-fold increase in the quantum yield of PVS^{\ominus} formation in the colloidal system ($\phi_{\text{max}} = 0.04$) relative to the homogeneous aqueous solution ($\phi_{\text{max}} = 0.003$) is observed. The enhanced electron transfer quantum yield in the colloidal system is attributed to the negatively charged particles that assist the separation of the photoproducts and retard their recombination due to electrostatic repulsion of one of the photoproducts. The significance of the negatively charged interface in retarding back-electron transfer of the photoproducts has been demonstrated by measuring the recombination rate constant of $\text{Ru}(\text{bipy})_3^{2+}$ and PVS^{\ominus} . In the SiO_2 colloidal system a substantial decrease in the recombination rate constant ($k_b = 1.5 \times 10^8 \text{ M}^{-1} \cdot \text{sec}^{-1}$) relative to the homogeneous system ($k_b = 3 \times 10^9 \text{ M}^{-1} \cdot \text{sec}^{-1}$) is observed. In addition, by increasing the ionic strength of the colloidal system the surface potential of the SiO_2 particles is decreased and, consequently, the quantum yield of the electron transfer process is reduced.

* The work described herein was sponsored by the Division of Chemical Sciences, Office of Basic Energy Sciences, Department of Energy, under Contract No. W-7405-ENG-48.

PHOTOSENSITIZED ELECTRON TRANSFER REACTIONS IN COLLOIDAL SiO_2 SYSTEMS:
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Sir:

Separation of products formed in photoinduced electron transfer processes is essential for efficient solar energy conversion.^{1,2} Several approaches involving systems such as functionalized micelles^{3,4}, liposomes^{5,6}, microemulsions⁷ and polyelectrolytes^{8,9} have been used as means to assist charge separation. In these processes the thermodynamically favored back reactions of the photoproducts can be retarded, and further utilization of the photochemical energy so stored to decompose water becomes feasible. Particular attention has been devoted to the photosensitized reduction of 4,4'-bipyridinium salts (viologens) by $\text{Ru}(\text{bipy})_3^{2+}$ and Zn-porphyrins^{10,11}. With these systems the photoreduction of water to hydrogen as well as photo-oxidation of water have been accomplished^{12,13}.

Here, we wish to report that an aqueous SiO_2 colloid provides a very effective solid-liquid interface that can retard the back reactions of properly chosen photoproducts. Consequently, high quantum yields in the photosensitized electron transfer processes are obtained.

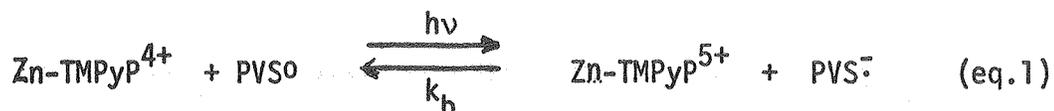
The colloidal SiO_2 suspension employed is composed of particles with a mean diameter of 40 Å. At pH >6 the particles are negatively charged and characterized by a high surface potential¹⁴. As a result, the interfacial system is capable of producing electrostatic attractions and repulsions with charged species formed in the photosensitized electron transfer. Thus, it should be possible to achieve the separation of products by these coulombic interactions. We have investigated the effect of the negatively

charged solid interface on the photosensitized reduction of propylviologen sulfonate, PVS^0 (1), by each of two positively charged sensitizers, Zn-meso-

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tetramethylpyridinium porphyrin, Zn-TMPyP⁴⁺, and Ru(bipy)₃²⁺. Triethanolamine TEA was used as the electron donor in the system. This electron donor ($E^0 = 0.82$ V) is irreversibly decomposed during its oxidation^{12a,b}.

The system is composed of an aqueous SiO₂ colloidal suspension, including PVS⁰ and Zn-TMPyP⁴⁺. The solution was deaerated with argon and illuminated at intervals of 15 seconds with a Xe-1000W lamp (light filtered through a CuSO₄ solution and Corning 3-72 and Corning 5-57 filters, $\lambda = 430-550$ nm, incident photon flux 5.0×10^{-7} einstein \cdot sec⁻¹). A rapid formation of the blue viologen radical (PVS⁻) was observed, and its rate of production was followed spectroscopically at $\lambda = 735$ nm ($\epsilon = 2500$ M⁻¹cm⁻¹), Figure 1(a). The initial quantum yield is $\phi_{\max} = 0.37$. Exclusion of the SiO₂ particles resulted in a significantly reduced rate of PVS⁻ production $\phi_{\max} = 0.038$, Figure 1(b). The dramatic enhancement of the electron transfer process quantum yield in the colloidal system (10-fold) is attributed to the presence of negatively charged particles, which assist the separation of the photoproducts and retard their recombination (Figure 2). The positively charged sensitizer (Zn-TMPyP⁴⁺) is adsorbed to the surface of the particle by coulombic attractions¹⁵. Electron transfer to the neutral zwitterionic acceptor (1) results in formation of the oxidized sensitizer, Zn-TMPyP⁵⁺, and the negatively charged acceptor, PVS⁻ (eq.1). The negatively charged silica particles (surface potential ca. -170 mV)¹⁵ eject the reduced acceptor into the bulk aqueous phase, thus retarding its recombination with Zn-TMPyP⁵⁺. The oxidized sensitizer is then available for the necessary oxidation of TEA. Replacement of the positively charged sensitizer with a negatively charged one would be expected to diminish the enhancing

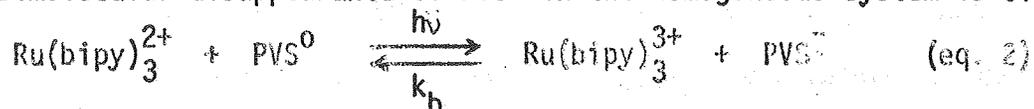


effect of the charged interface. Indeed, exchange of Zn-TMPyP^{4+} by $\text{Zn-meso-tetraphenylporphyrin sulfonate}$, Zn-TPPS^{4-} , gives in the colloidal system, a quantum yield ($\phi_{\text{max}} = 0.016$) very similar to that obtained in the corresponding homogeneous system ($\phi_{\text{max}} = 0.012$), Figure 1(c) and (d). Thus, repulsion of the two negatively charged photoproducts by the SiO_2 particles allows a recombination rate similar to that present in the homogeneous solution.

The role of the surface potential in affecting the quantum yield of the electron transfer process was confirmed by varying the ionic strength of the reaction medium. Increasing the ionic strength is expected to decrease the surface potential of the particles^{15,16}, and, consequently, reduce the quantum yield. At an ionic strength of 0.5 M NaCl the quantum yield of PVS^- production drops to $\phi_{\text{max}} = 0.07$ (Figure 3). This result indicates that at high ionic strength, association of the positive sensitizer with the interface is reduced. As a result, only a fraction of the sensitizer is active in the interfacial process, while most of it reacts in the bulk aqueous phase.

The enhancing effect of the SiO_2 particles on the quantum yield is similar in a system that includes the positively charged Ru(bipy)_3^{2+} instead of Zn-TMPyP^{4+} as sensitizer. A colloidal suspension of 0.1% SiO_2 particles containing Ru(bipy)_3^{2+} (7.6×10^{-5} M), PVS^0 (1×10^{-3} M) and TEA (10^{-3} M) at pH = 9.6 was deaerated and illuminated under the conditions previously described. The quantum yield for the photosensitized production of PVS^- in the interfacial system ($\phi_{\text{max}} = 0.04$) appears to be 13-fold that of the corresponding homogeneous system ($\phi_{\text{max}} = 0.003$).

A flash photolytic study performed with the system that includes $\text{Ru}(\text{bipy})_3^{2+}$ as sensitizer has conclusively established the activity of the negatively charged interface in retarding the recombination of photoproducts (eq. 2). The bimolecular disappearance of PVS^- in the homogeneous system is close



to that of a diffusion controlled process ($k_b = 3.6 \times 10^9 \text{ M}^{-1} \cdot \text{sec}^{-1}$). In the colloidal SiO_2 system a substantial decrease in the recombination rate is observed ($k_b = 1.5 \times 10^8 \text{ M}^{-1} \cdot \text{sec}^{-1}$). Here, again, the negatively charged interface retards back electron transfer.

In conclusion, we have demonstrated that the introduction of the solid interface SiO_2 can affect strongly the efficiency of the photosensitized electron transfer process. By proper charge functionalization of the electron acceptor and donor, electrostatic repulsive or attractive interactions can be established. The high charge-density of the colloidal SiO_2 particles provides a driving force for charge separation and diminishes back reactions. The stabilized intermediary photoproducts might then be further coupled with efficient reactions that result in the decomposition of water. These aspects are currently being investigated.

Acknowledgment: The work described herein was sponsored by the Division of Chemical Sciences, Office of Basic Energy Sciences, Department of Energy under contract W-7405-ENG-48.

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15. By using a positively charged spin label it has been confirmed independently that the positive species interacts with the negative SiO₂ interface. The sharp ESR signal of the spin label in a homogeneous

aqueous solution becomes very broad upon addition of SiO_2 particles. Increasing the ionic strength of the colloidal system results in the reappearance of the sharp signal characteristic of homogeneous solution. Based on the number of ionized sites on the particle a value of ca. -170 mV for the surface potential has been calculated. A comprehensive correlation of surface potential with the observed photosensitized electron transfer process as well as the binding constant measurements of $\text{Ru}(\text{bipy})_3^{2+}$ to the SiO_2 particles will be published elsewhere.

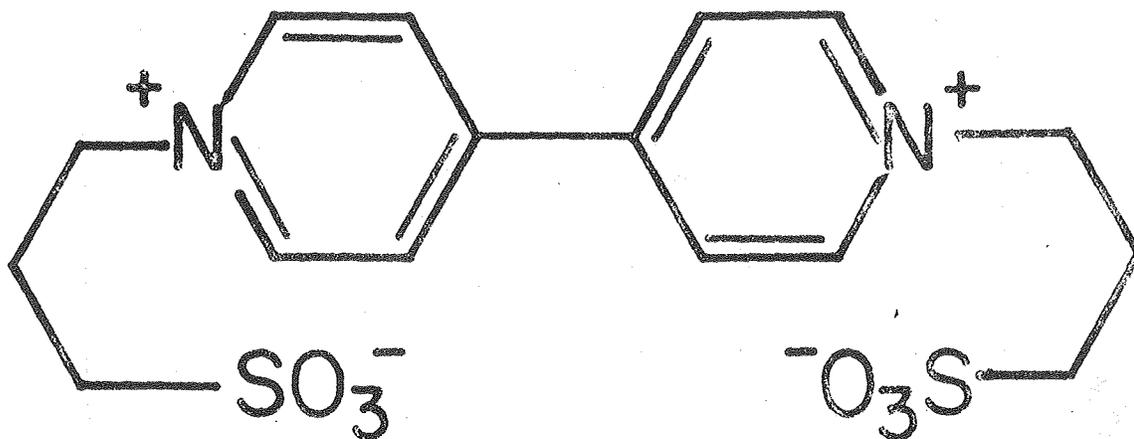
16. In ref. 14, Chapter 5, p. 108.

Figure Captions

Figure 1 Propylviologen radical, $PVS^{\cdot-}$, formation as a function of light absorbed. All experiments at pH = 10.2 $[PVS^0] = 2 \times 10^{-3}$ M, $[TEA] = 1 \times 10^{-2}$ M. (a) 0.1% SiO_2 colloidal system, sensitizer Zn-TMPyP $^{4+}$ $[3.5 \times 10^{-6}$ M]. (b) Homogeneous aqueous solution, sensitizer Zn-TMPyP $^{4+}$ $[3.5 \times 10^{-6}$ M]. (c) 0.1% SiO_2 colloidal system, sensitizer Zn-TPPS $^{4-}$ $[9.2 \times 10^{-6}$ M]. (d) Homogeneous aqueous solution, sensitizer Zn-TPPS $^{4-}$ $[9.2 \times 10^{-6}$ M].

Figure 2 Schematic function of SiO_2 particles in photosensitized electron transfer process

Figure 3 Propylviologen radical, $PVS^{\cdot-}$, formation as a function of ionic strength of the system. Experiments at pH = 9.8, $[PVS^0] = 1 \times 10^{-3}$ M, $[TEA] = 1 \times 10^{-3}$ M; sensitizer Zn-TMPyP $^{4+}$, 4×10^{-6} M. (a) $[NaCl] = 0.002$ M; (b) $[NaCl] = 0.1$ M. (c) $[NaCl] = 0.5$ M.

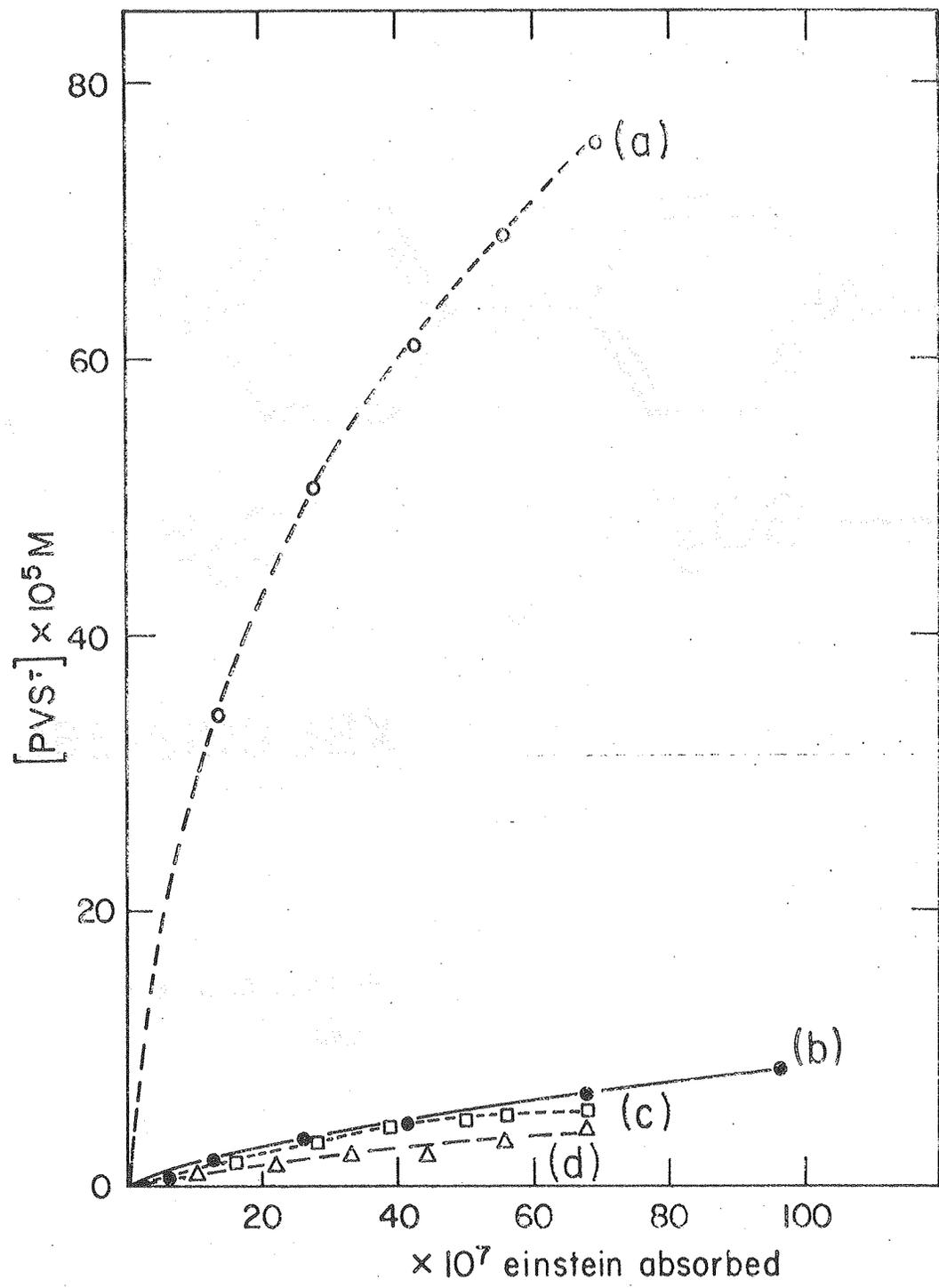


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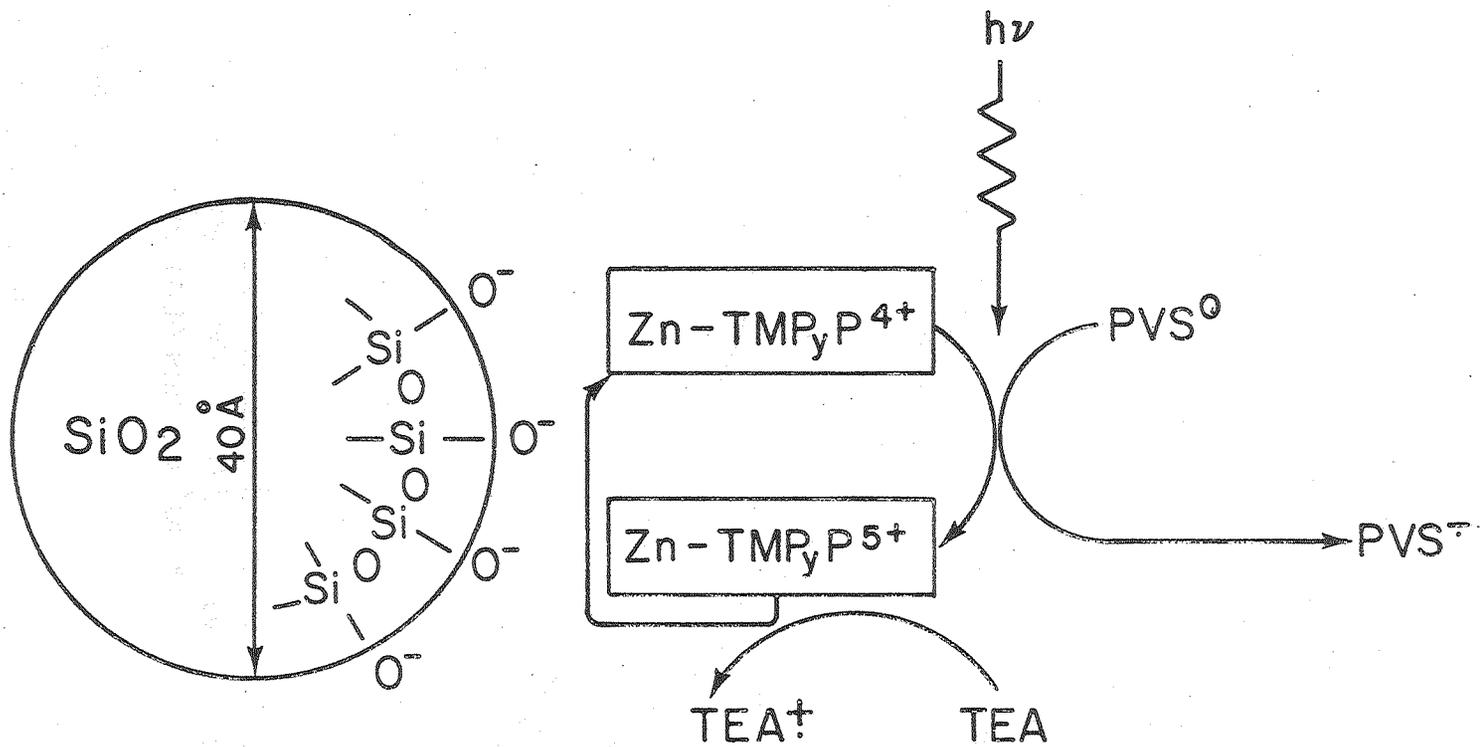
FORMULA



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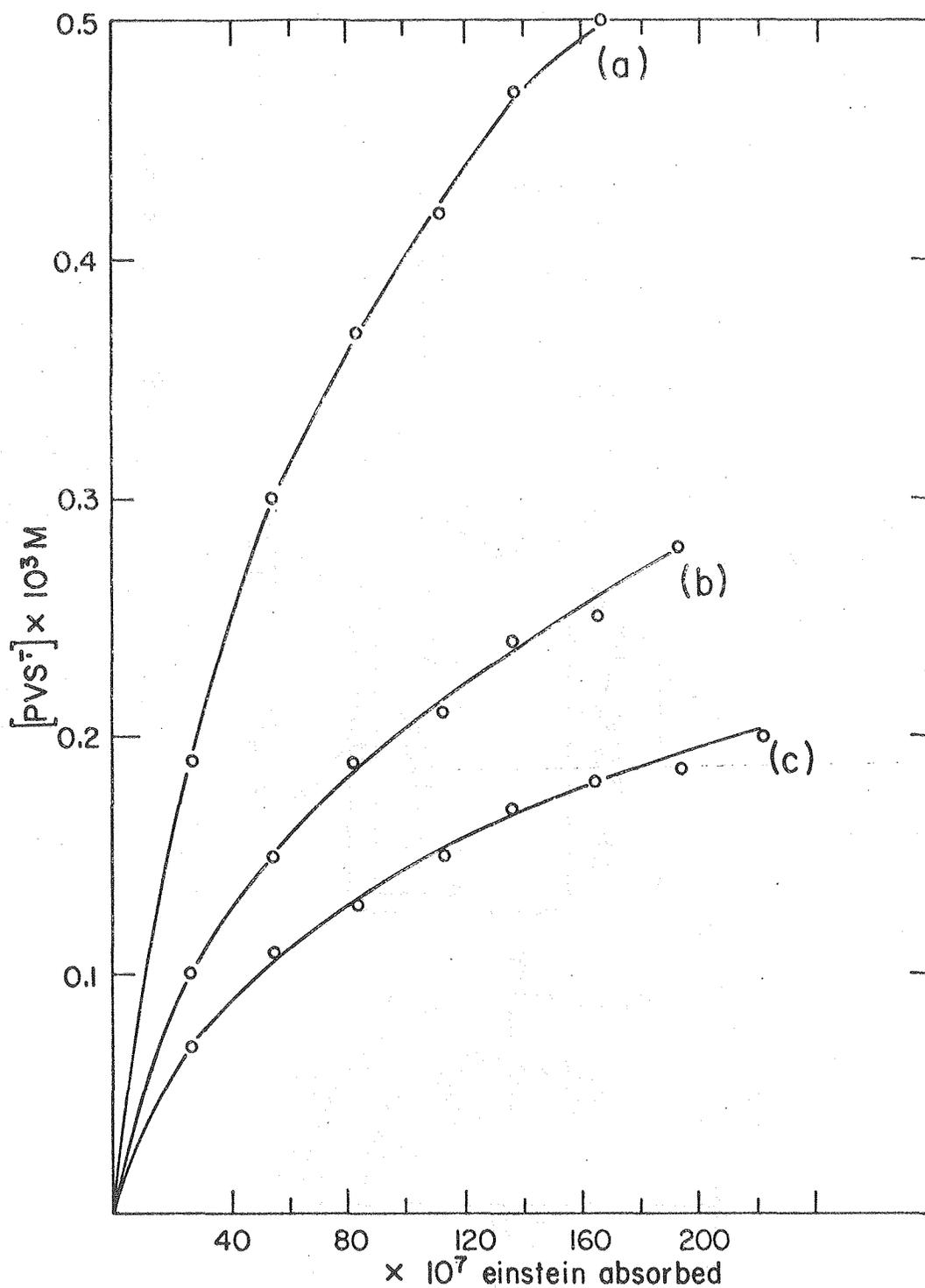
FIGURE 1



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FIGURE 2



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FIGURE 3