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ASPECTS OF ARTIFICIAL PHOTOSYNTHESIS IN SURFACTANT VESICLES*

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Summary

Advantage has been taken of the separate compartments provided by completely synthetic surfactant vesicles to organize the sensitizers, donors and acceptors needed for photochemical solar energy conversion. Chemically dissymmetrical polymerized surfactant vesicles proved to be particularly useful media for membrane-mimetic photochemistry. Efficient charge separation followed by electron transfer across the bilayer of the vesicle and hydrogen generation have been demonstrated. Details of these systems are discussed critically.

Photochemical investigation of systems which mimic membrane functions is an extremely active area of current research. Micelles [1], monolayers [2], bilayers [3] and vesicles [4 - 13] have been the most-exploited membrane-mimetic agents.

Figure 1 shows schematic representations of the organized structures formed by surfactants in different media. It is important to recognize that these structures are an artist's renderings of our conceptions and are based mostly on indirect observations. Research in membrane-mimetic chemistry has two main objectives. The first objective is to obtain a better and more detailed understanding of biological membranes. Indeed, luminescence probes have been used extensively for assessing microenvironments and the structural and dynamic characteristics of membranes and model systems [14]. The second objective is the development of novel photochemistry based on membrane-mediated processes and its utilization for practical purposes. Potential applications include the stabilization of excited states and spectroscopic examination (*e.g.* room temperature phosphorescence [15]), synthesis [16], isotope separation [17] and solar energy conversion and storage [18]. Solar energy conversion and storage in completely synthetic surfactant vesicles is the subject of the present paper.

Photochemical solar energy conversion is a vitally important and extremely active area of research [19 - 26]. The excited state of a suitable sensitizer, produced by irradiation, is a better electron acceptor as well as a better electron donor than the ground state of the sensitizer. Light absorption can therefore

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drive a redox reaction non-spontaneously and result in the storage of energy ΔG in D^+ and A^-; this is shown in Fig. 2. Further, if D^+ and A^- have appropriate redox potentials they may directly reduce water to hydrogen and oxidize it to oxygen:

$$2A^- + 2H_2O \rightarrow 2A + 2OH^- + H_2\uparrow \qquad 2e^- \text{ reduction} \qquad (1)$$

$$4D^+ + 2H_2O \rightarrow 4D + 4H^+ + O_2\uparrow \qquad 4e^- \text{ oxidation} \qquad (2)$$

Unfortunately, in homogeneous solution the rapid recombination of $D^+ + A^-$ to $D + A$ precludes the possibility of this type of photochemical energy storage and conversion. Separation of charges in space provides an efficient method for diminishing undesirable charge recombinations. Effective charge separation has been demonstrated in surfactant vesicles [4 - 13]. Surfactant vesicles are expected (a) to solubilize, to concentrate, to compartmentalize, to organize and to localize reactants, (b) to maintain proton and/or reactant gradients, (c) to alter quantum efficiencies, (d) to reduce ionization potentials, (e) to change oxidation and

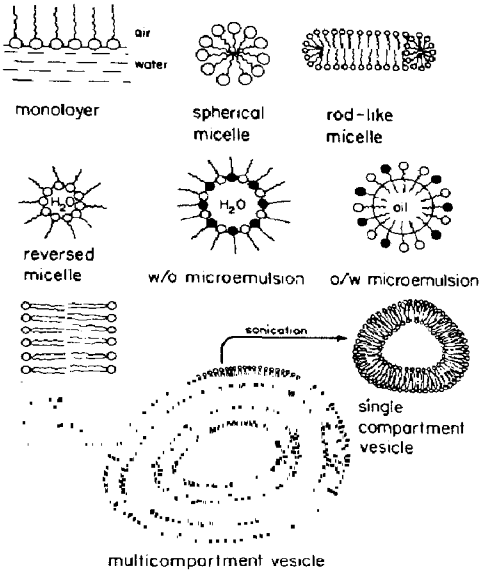


Fig. 1. An oversimplified representation of organized structures of surfactants in different media.

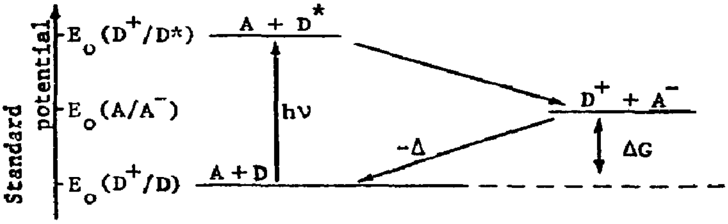
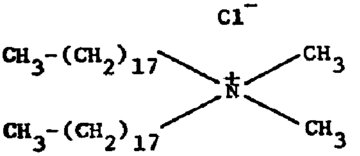


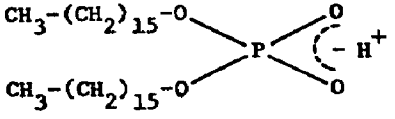
Fig. 2. A non-spontaneous light-driven redox reaction which results in energy storage.

reduction properties, (f) to change dissociation constants, (g) to affect vectorial electron displacements, (h) to alter photophysical pathways and rates, (i) to alter chemical pathways and rates, (j) to stabilize reactants and/or products and/or transition states, (k) to separate charges and/or products and (l) to be chemically stable, optically transparent and photochemically inactive.

Most of our investigations to date have utilized dioctadecyldimethylammoniumchloride (DODAC) and dihexadecylphosphate (DHP):



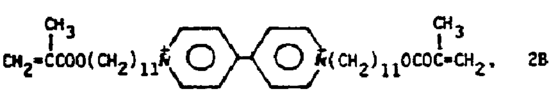
DODAC



DHP

Dispersal of DODAC or DHP in water by ultrasonic irradiation results in the formation of fairly uniform single-compartment vesicles. DODAC and DHP vesicles are stable for weeks in the pH 2 - 12 range, are osmotically active, undergo thermotropic phase transitions and, most importantly, entrap and retain molecules in their compartments. The advantages of surfactant vesicles with respect to other systems are that they are able to organize large numbers of sensitizers, electron donors and acceptors per aggregate and that they are amenable to electrostatic modification and chemical functionalization. An important property is that, unlike natural membranes which are composed mostly of zwitterionic lipids, surfactant vesicles are highly charged and have high charge densities on their surfaces.

Recognizing the need for enhanced stability and controlled permeabilities, we have synthesized a number of polymerized redox-active surfactant vesicles [27, 28]. Typical structures of vesicle-forming surfactants are the following:



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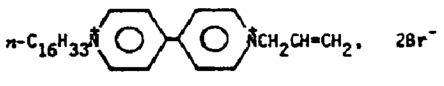

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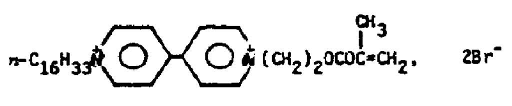

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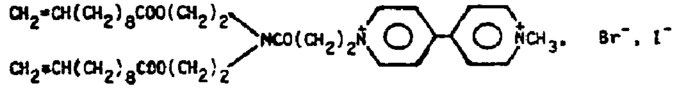

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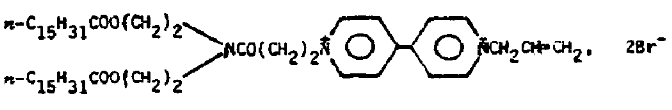

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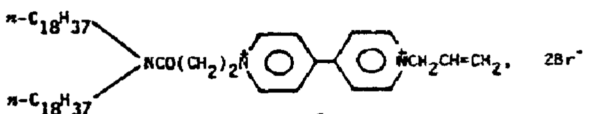

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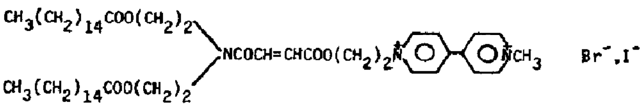

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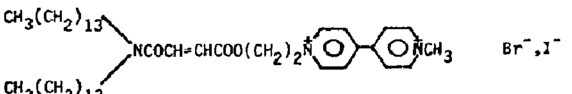

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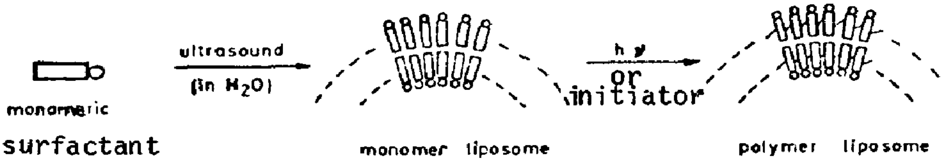
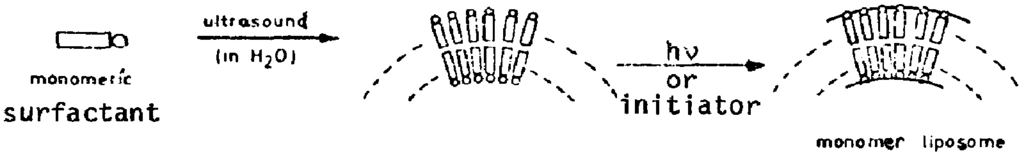
On sonication, surfactants **1** - **8** undergo vesicle formation; the vesicles can be polymerized by an initiator or by UV irradiation across either their bilayers or their head-groups depending on the position of the double bond:





Polymerized vesicles remain stable for extended periods even in 25% C_2H_5OH. Like their unpolymerized counterparts, they are able to organize molecules, to retain their osmotic activities and to undergo thermotropic phase transitions.

Photosensitized electron transfer from the tris(2,2′-bipyridine)ruthenium cation ($Ru(bpy)_3{}^{2+}$) to methylviologen (MV^{2+}) has been investigated in the presence of negatively charged DHP surfactant vesicles by steady state photolysis, fluorescence quenching and nanosecond laser flash photolysis [9]. Four different substrate–surfactant vesicle organizations have been used (Fig. 3). In system I, $Ru(bpy)_3{}^{2+}$ was attached to the outer surfaces and MV^{2+} was placed on the inner surfaces of DHP vesicles. In system II, MV^{2+} was attached to the outer surfaces and $Ru(bpy)_3{}^{2+}$ to the inner surfaces of DHP vesicles. In system III, both $Ru(bpy)_3{}^{2+}$ and MV^{2+} were localized on the outer surfaces of DHP vesicles. In system IV, both $Ru(bpy)_3{}^{2+}$ and MV^{2+} were localized on the inner surfaces of DHP vesicles. Extremely efficient electron transfers have been observed on the surfaces of surfactant vesicles in systems III and IV. Electron transfer from excited $Ru(bpy)_3{}^{2+}$ to MV^{2+} across the bilayers of vesicles in the presence of externally added ethylenediaminetetraacetic acid (EDTA) in system I resulted in the formation of reduced methylviologen $MV^{\cdot +}$ at up to 75% conversion with a quantum efficiency of 0.26. If additionally about 10^{-5} M PtO_2 was entrapped in the interiors of the DHP vesicles in system I, $MV^{\cdot +}$ promptly re-formed with

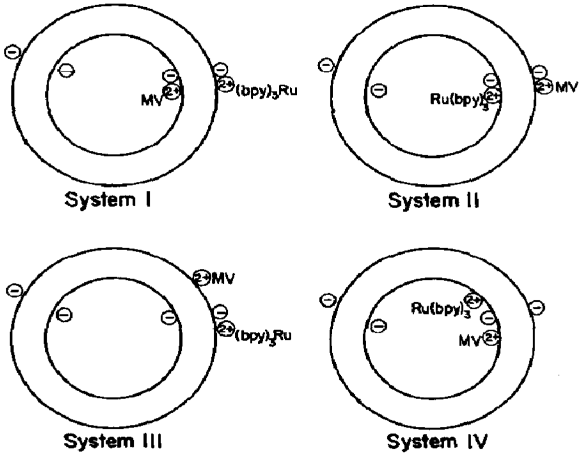


Fig. 3. Schematic diagrams of the different DHP surfactant vesicle–sensitizer–acceptor systems used.

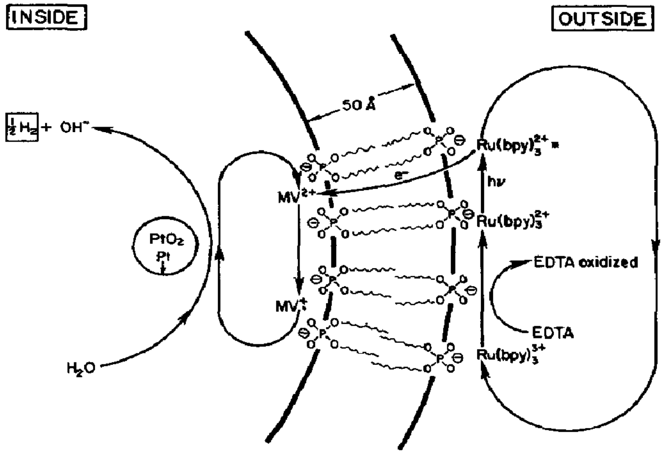


Fig. 4. Schematic diagram of the surfactant vesicle system used for photosensitized catalytic hydrogen production; the photolysis results in the consumption of EDTA only.

concomitant hydrogen evolution. Photolysis of this system leads to the net consumption of only EDTA at very low stoichiometric $Ru(bpy)_3{}^{2+}$, MV^{2+} and PtO_2 concentrations (Fig. 4).

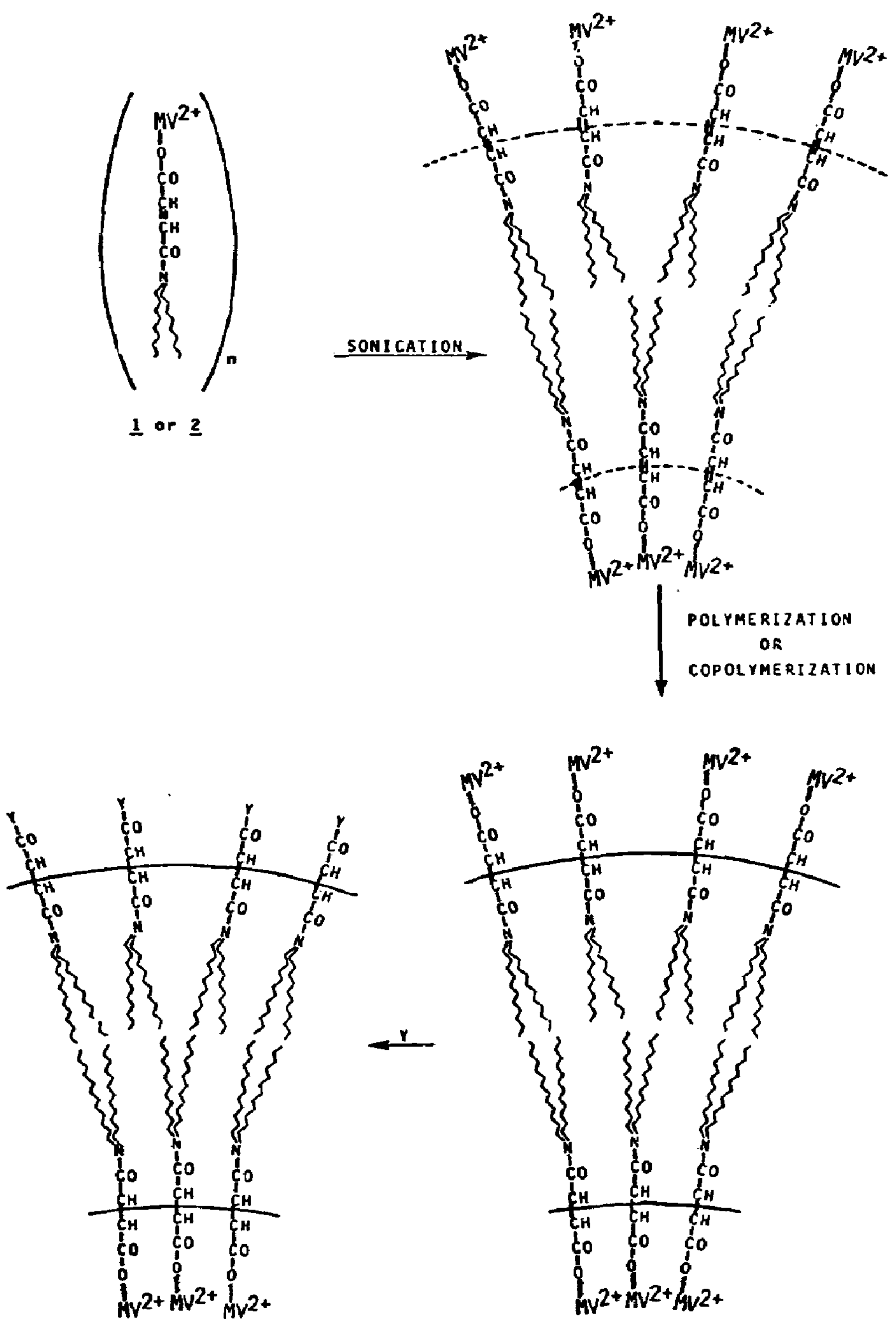


Fig. 5. Illustration of the proposed formation of polymeric surfactant vesicles in which the outer redox-active viologen groups have been removed by nucleophilic cleavage of the ester bond.

Greater efficiency of charge separation has been realized in chemically dissymmetrical polymerized surfactant vesicles prepared from **5** and **6** (Fig. 5). Photoexcitation of $Ru(bpy)_3{}^{2+}$ placed on the outside of dissymmetrical **5** resulted in electron transfer from $Ru(bpy)_3{}^{2+*}$ across the bilayers to give long-lived reduced viologens. Full exploitation of this and related systems in photochemical energy conversion is under active investigation in our laboratories.

Acknowledgment

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