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# Physical and Chemical Studies of Chlorophyll in Microemulsions

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# ABSTRACT

We have been conducting studies designed to provide fundamental information on both the nature of photoreactions in microemulsions and the utility of these media as solvents for absorbers of solar energy. As a test system, we investigated the photoreduction of absorbed dye (principally methyl red) sensitized by chlorophyll a in an anionic mineral oil in water microemulsion. Using ascorbate as the water soluble reducing agent and pigment concentrations of up to eight per drop (10mM), the reaction exhibits a pseudo zero order dependence on methyl red. The effect of sensitizer, ascorbate concentration and light intensity on the quantum yield was examined, as well as the effect of varying the microemulsion charge type, product catalysis, and the use of synthetic porphyrin sensitizers. In microemulsions containing up to eight chlorophyll molecules per microdroplet, the quantum yield remains constant over five orders of magnitude concentration. The intrinsic quantum yield is independent of droplet surface charge, but is dependent on pH. One of the products of the chemical reduction of methyl red, N,N-dimethyl-p-phenylenediamine (DMPD), increases the limiting quantum yield two to three fold.

Synthetic porphyrins have been found to act as sensitizers, and a number of tetrapyridyl porphin derivatives containing one to four carbon chains of varying length have been made and examined. The results show that the quantum yield increases with increasing chain length for the monoalkyl compounds, and also indicate the possble involvement of a sensitizer orientation effect. The transport of oil soluble electroactive species in nonionic microemulsions have been found to exhibit percolation behavior, which has potential photogalvanic applications.

## Introduction

The overall objective of this work is to investigate the utility of microemulsions as solvent media for absorbers of solar energy which can act as photosensitizers of redox reactions. These studies will provide fundamental information on the nature of interactions and (photo) reactions at microscopic oil-water interfaces, as well as a basis for photochemical energy conversion methods. To this end, we have employed the chlorophyll mediated photoreduction of dyes, pincipally methyl red, by ascorbate in oil in water (o/w) micellar emulsions as our model system.

Previous work (1) has shown that chlorophyll dissolved in ananionic oil/water microemulsion degrades slowly under white light irradiation, but is protected by the presence of a redox system or couple such as azobenzene/hydrazobenzene. Because of its structure, and thus solubility characteristics, the chlorophyll is located in the surface region of the microroplet. It was anticipated therefore that at high local pigment concentration, aggregation might lead to enhanced quantum yields (2).

Initial studies have been designed to provide basic information on sensitized photoreaction in microemulsions. The photoreduction of methyl red and crystal violet has been examined in a sodium cetyl sulfate/pentanol/mineral oil o/w system. Using ascorbate as the water soluble reducing agent and pigment concentrations of less than one per drop ($\leq 10$ μM), the reaction was found to exhibit a pseudo first order dependence on crystal violet, but a pseudo zero order dependence on methyl red. The effect of sensitizer, ascorbate concentration and light intensity on the quantum yield has also been examined (3). From the results of these and auxiliary studies, a reaction mechanism is proposed which involves the formation of a chlorophyll-dye triplet exciplex rather than any direct intermediacy of an oxidized or reduced pigment species. Based on this scheme, a number of rate constants have been estimated (4).

Most of the earlier work was performed using an anionic microemulsion employing sodium cetyl sulfate (SCS) as the surfactant. Investigations have now been extended to cationic cetyltrimethylammonium bromide (CTAB) and nonionic (Brij 96) systems. The composition of these micellar emulsions are given in Table 1. Phase maps on the SCS (5), CTAB (6) and Brij 96 (7) systems are available.

Previous measurements of chlorophyll a in the anionic SCS microemulsion (2,8) indicated that at high pigment concentration (greater than one sensitizer molecule per microdroplet) the quantum yield of the methyl red-ascorbate reaction increased, although there was no apparent change in the chlorophyll absorption spectrum. Additional detailed and painstaking concentrated spectra were obtained using a much thinner spacer, and there is definately no difference between the dilute and concentrated chlorophyll spectra. Using a Brij 96 microemulsion, it has now been shown that the quantum yield is independent of pigment concentration up to at least eight molecules per drop (9).

The kinetics of the chlorophyll-sensitized photoreduction of methyl red by ascorbate were examined in oil-in-water microemulsions stablized by nionic (SCS), cationic (CTAB), and nonionic (Brij 96) surfactants (10). The results show that the intrinsic quantum yield is essentially unaffected by microemulsion charge type. The effect of surface potential is to control the minimum ascorbate concentration needed to achieve saturation. There is an indirect effect on limiting quantum yield via the effect of charge type on surface pH. The decreasing quantum yield with increasing pH is ascribed to an effect on the yield of triplet chlorophyll (11). In addition, the chlorin sensitized photoreduction of methyl red (but not crystal violet) is found to be catalyzed by the reaction product N,N-dimethylphenylenediamine (11, 12).

Recently, examination of various synthetic porphyrins were initiated (9). These compounds, which include some surfactant porphyrins, have also been found to act as senitizers.

## Scope.

A variety of synthetic porphyrins were synthesized, and some examined for their efficacy as sensitizers of the methyl red/ascorbate test reaction. Electro-chemical studies were initiated to serve as a basis for photogalvanic studies. Apparatus for flash photolysis experiments is being assembled. The third funding period is from 12/1/79 - 11/30/80. We report here our progress as of 11/30/80.

## Results.

The compositions of the microemulsions employed are given in Table 1.

TABLE 1. Initial Composition of Microemulsions.*

| Charge Type | Oil | Surfactant (weight %) | Cosurfactant (wt. %) |
|---|---|---|---|
| anionic | mineral oil | sodium cetyl sulfate (SCS) (40) | n-pentanol (60) |
| neutral | hexadecane | polyoxyethylene 10 oleyl ether (Brij 96) (66) | n-butanol (34) |
| cationic | hexadecane | cetyl trimethylammonium bromide (CTAB) (50) | n-butanol (50) |
| neutral | hexadecane | Tween 60 (66) | n-pentanol (34) |

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*Initial composition consisting of specified amount of oil and emulsifier (surfactant plus cosurfactant) which is then diluted with water or aqueous buffer.

I. Synthetic porphyrin sensitizers. Since chlorophyll and pheophytin were found to exhibit similar quantum yields, studies were extended to other synthetic porphyrins. A few were available from various sources, and several surfactant porphyrins were synthesized according to a modified procedure of Okino, et al. (13). These preliminary results are summarized in Table 2, and give rise to some interesting possibilities. There are four possible factors which can influence the quantum yield; the charge, location and orientation (in the interphase) of the sensitizer, as well as steric hindrance (by the sensitizer alkyl chains) to approach of the oxidant. The data in homogeneous solution (95% ethanol) seem to rule out the steric effect. The charge effect seems to yield a maximum factor of three (monoethyl to tetramethyl). The average location of the porphyrin in the interphase must certainly be a factor since it can influence both the effective ascorbate concentration and the medium polarity. The precise result of this effect is not clear at present since the monoeicosyl quantum yield is greater than that of the monothyl by a factor of 1.5, while q for the tetramethyl exceeds that of the triomethylmonocetyl by a factor of 2. There remains nonetheless reasonable evidence for the existence of an orientation effect (14), since the tricetyl is well over an order of magnitude less than the monocetyl. Even after "correcting" for charge, q is still a factor of 5 higher for the latter. In addition, based purely on geometric considerations, the major "break" in q is expected to come after the diceytyl derivative, as observed. This intriguing possibility certainly requires additional investigation. One possibility is to

Table 2. Quantum yields for the photoreduction of methyl red by ascorbate sensitized by tetrapyridylporphins derivatives.

| Sensitiers (charge)[a] | Brij 96[b] | 95% ETOH[c] | DMF[c] |
|---|---|---|---|
| monoethyl (+1) | 0.21 | ---- | ---- |
| monododecyl (+1) | 0.26 | ---- | ---- |
| monocetyl (+1) | 0.27 | 0.10 | .008 |
| monoeicosyl (+1) | 0.32 | ---- | ---- |
| dicetyl (+2)[d] | 0.19 | ---- | .006 |
| tricetyl (+3) | 0.02 | 0.09 | ---- |
| tetracetyl (±4) | <.02 | ---- | ---- |
| tetramethyl (+4) | 0.065 | ---- | ---- |
| trimethylmonocetyl (+4) | 0.033 | ---- | ---- |

a. The sensitizer is produced by alkylation of the pyridine nitrogen(s) of meso tetra-(4-pyridyl) phorphine.

b. Brij 96 microemulsion, 60% water, 6mM ascorbate.

c. 95% ethanol or dimethlformamide, containing 6mM ascorbic acid.

d. possible mixture of two isomers.

use an oil soluble reducing agent in place of ascorbate to probe the contribution of location. Finally, it should be noted that the quantum yield of 30% for the long chain monalkyl derivatives is three times greater than that for chlorophyll, and the largest observed in this system to date.

II. Transport studies. We have also been interested in the transport properties of species in the microemulsion, and have performed a number of electrochemical studies toward that end. These studies include conductance (5, 15, 16), specific ion (15, 17) and diffusion coefficient (15, 16) measurements. Charged droplets in cationic or anionic microemulsions have essentially concentration independent diffusion coefficients (D). The values of D are in the 4-8 x $10^{-7}$ $cm^2s^{-1}$ range as expected from their radii and the Stokes-Einstein equation. However, in nonionic microemulsions a very different situation is observed, as indicated in Figure 1. The decreasing diffusion coefficient (D) with decreasing phase volume ($\phi$) may result from a percolative type of phenomenon hitherto only observed in reverse (w/o) microemulsions (18). Aqueous species on the other hand exhibit the expected increasing D with decreasing $\phi$ (16). These microemulsion may have a potentia application as photogalvanic cell fluids since $\phi$ can be adjusted to carry oil and water soluble (reacted) species toward opposite electrodes at selected rates. For example, consider a thin cell containing an optically dense solution, an oil soluble acceptor and a water soluble donor. The sensitizer(s)

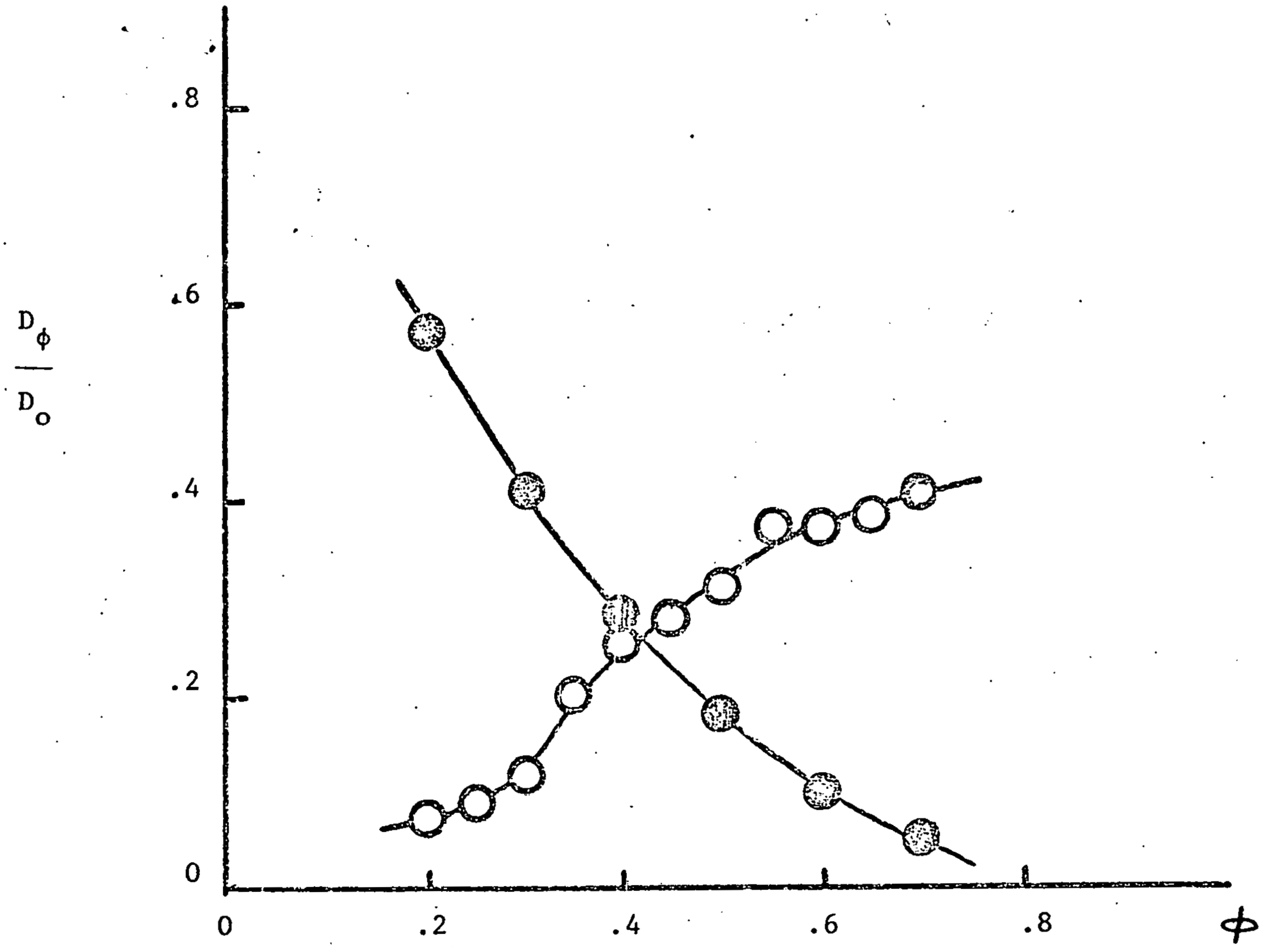

Figure 1. Ratio of diffusion coefficient in a nonionc T ween 60/pentanol/hexadecane (7% initial w/w) o/w microemulsion ($D_\phi$) to that in water ($D_o$) for droplets (open circles) and aqueous ions (closed circles).

is(are) also located in the drop. If the sample is irradiated through a transparent semiconductor electrode (e.g., n type), then at low $\phi$ the aqueous ion can reach the opposite (nonilluminated) electrode as the droplet acceptor reaches the semiconductor electrode. This also facilitates rapid charge separation. The n-type electrode will tend to act as the anode, and may possibly be made more selective to the drop species (here the acceptor) by derivitization (19,20) or hydrophobic coating. The same reasoning can be applied to other electrode/redox couple combinations. These electrochemical studies are being continued to provide input to planned photogalvanic experiments.

III. Other Studies. We have synthesized the tetra methyl and tetra cetyl esters of tetra-(4-carboxyphenyl) porphin, and are currently working on the synthesis of several other porphyrins. We have assembled and are testing the equipment for performing photogalvanic studies, and are in the process of setting up the apparatus for flash photolysis experiments.

Summary.

1. A number of synthetic porphyrin sensitizers containing hydrocarbon chains of varying length and number have been synthesized.

2. For the monoalkyl porphyrins, the quantum yield increases with increasing chain length.

3. There is an apparent decrease in quantum yield for three or four long alkyl chains on the sensitizer, which may indicate some contribution from an orientation effect.

4. Transport studies of the diffusion of oil soluble species have been carried out in ionic and nonionic microemulsions. Percolation type behavior have been observed for the latter, and has potential application to photogalvanic studies.

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