Reports

Carrier-Mediated Photodiffusion Membranes

Abstract. *Reversible photochromic reactions can be coupled to carrier-mediated transport processes in membranes to bring about the separation or concentration of selected permeants. Carbon monoxide has been pumped against a fourfold concentration gradient by differentially illuminating a hemoglobin membrane. The extent of concentration of photochromic ligands increases with light intensity and is reversible. Nonphotochemically sensitive ligands can also be transported by coupling with photosensitive carrier-mediated systems.*

By taking advantage of carrier-mediated diffusion—reversible reactions of permeants in membranes—it has been demonstrated that transport rates can be enhanced, specific separations accomplished, and concentration of selective species achieved (*1*). In the past these effects were produced by means of concentration driving forces. Here we show how reversible photochemical reactions (photochromic reactions) can similarly be coupled to membrane processes to modulate diffusion rates and to concentrate permeants.

When a substance can reversibly react with another substance which is confined to a film or membrane, carrier-mediated diffusion can occur. For example, if a layer of hemoglobin solution is exposed to oxygen, the O_2 can dissolve in the membrane and react to form oxyhemoglobin complexes. The net flux of O_2 across the film is enhanced by the formation of O_2 complexes, which also serve to transport O_2 through the film (*1*). Calculation of fluxes in systems of this type can become very complex, and some methods of dealing with these problems have been reviewed (*2*). A good deal of insight into the phenomena can be gained by considering only the limiting situation where reaction rates are much faster than diffusion rates—that is, the reaction-equilibrium state (*3*)—which is usually much simpler from a mathematical point of view.

For example, for the membrane reaction

$$A + B \underset{l_2}{\overset{l_1}{\rightleftarrows}} AB$$

where the carrier B and complex AB are confined to the membrane phase and have equal diffusivities ($D_B = D_{AB}$), the transport of permeant A (N_A moles per square centimeter per second) across the membrane (of thickness d) from side I to side II is given by (*3*)

$$N_A = \frac{D_A}{d}([A]_I - [A]_{II}) + \frac{D_{AB}[B]_t}{d} \times \left(\frac{[A]_I}{L_I^{-1} + [A]_I} - \frac{[A]_{II}}{L_{II}^{-1} + [A]_{II}} \right) \quad (1)$$

where square brackets denote concentration, $[B]_t$ is the total concentration of carrier in the membrane, and $L = l_1/l_2$ is the association constant of the carrier-permeant complex, where l_1 and l_2 are the forward and reverse kinetic constants.

In most previous analyses of carrier-mediated transport (*2–4*), it has been assumed that l_1 and l_2 are the same everywhere within the membrane phase. However, there is a class of photochemical reactions where the kinetic constants are a function of light intensity [for example, in the reaction of CO with myoglobin, l_2 increases with light intensity (*5, 6*)]. For these reactions, the boundary concentration of the permeant-carrier complex can be affected by variations in light intensity

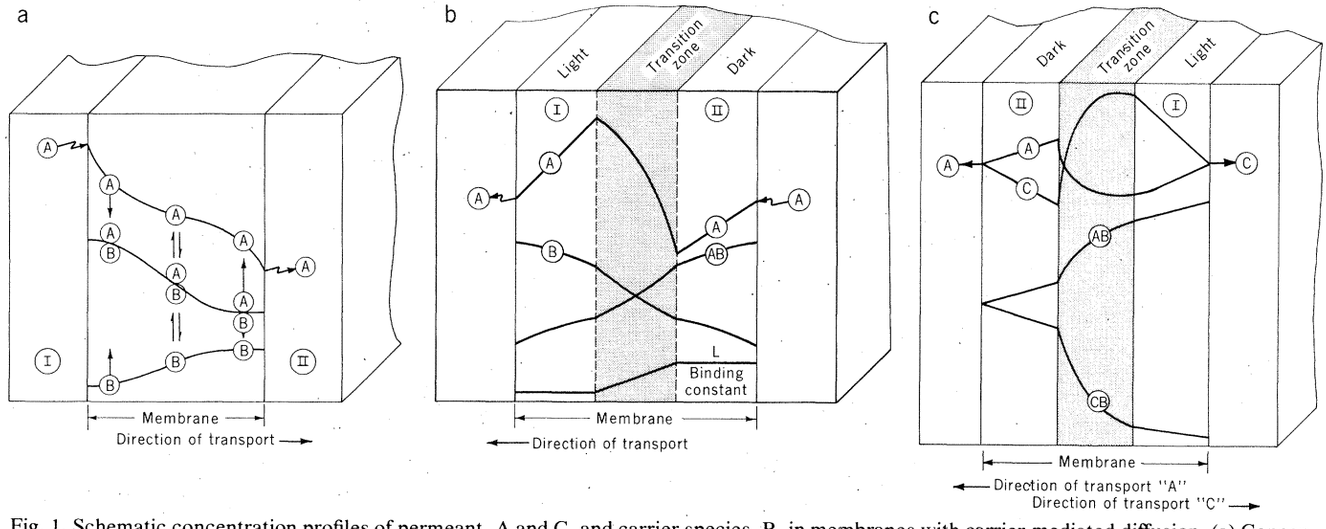

Fig. 1. Schematic concentration profiles of permeant, A and C, and carrier species, B, in membranes with carrier-mediated diffusion. (a) Concentration profiles for the situation where the entire membrane is uniformly illuminated or dark. Transport of the permeant, A, is down its concentration gradient. (b) Concentration profiles in a membrane where the illumination is not uniform. Chamber I is illuminated and the binding constant, L, is reduced in this section of the membrane. Transport of the permeant takes place even though there is no net concentration difference across the membrane. (c) Indirect photodiffusion membrane. The binding of permeant A is not light-sensitive in this example but the binding of permeant C is light-sensitive. Because of competition with the carrier, A is transported across the membrane in the absence of a net concentration difference. The graphs are not to scale.

throughout the membrane, as well as by other factors, and therefore through this photochemical mechanism the magnitude and direction of the flux of permeant across the membrane can be modified by light intensity.

If the affinity between permeant and carrier is the same everywhere, $L_I = L_{II}$. Then from Eq. 1, if $[A]_I > [A]_{II}$, the flux of the permeant across the membrane will be in the direction I → II, and the flux will be facilitated by the additive contribution of the second term (the carrier-mediated component) to the first term (Fick's law) as shown in Fig. 1a.

But if $L_I \neq L_{II}$, the second term in Eq. 1 may be negative and greater in magnitude than the first term, predicting a flux of permeant against its own concentration gradient. This possibility can be realistically achieved for photochromic reactions.

The reversible photodissociation of CO and hemoproteins is well known (*5, 6*) and is used here to demonstrate the phenomena of light-modulated transport by the configuration shown in Fig. 1b. The "membrane" consisted of a sandwich of a porous silver disk between two filter-paper disks that were wetted with a hemoglobin solution. This arrangement allowed free diffusive communication between both sides of the membrane while preventing light from one side from penetrating to the other side. At time zero, tracer ^{14}CO was admitted to the downstream reservoir chamber while both sides of the membrane were dark. The first portion of the graph in Fig. 2a shows the diffusion of CO across the hemoglobin film, which is presumably facilitated as previously reported by Mochizuki and Forster (*7*). After equilibrium was attained, the upstream side of the membrane was illuminated and an accelerated CO transport into the upstream chamber commenced; this continued until a new steady state was achieved in which the concentration of CO in the illuminated chamber was about twice the reservoir concentration. When the light was turned off, CO diffused back to the reservoir, down its concentration gradient. The process was repeatable and could be modified by changing the intensity of illumination, as shown in Fig. 2b (*8*).

Table 1. Calculated concentration of CO by a photodiffusion membrane. Assumptions: $D_{CO} = 1.5 \times 10^{-5}$ cm²/sec; $D_{MbCO} = 7.0 \times 10^{-7}$ cm²/sec; $[Mb]_t = 8.33 \times 10^{-3} M$; $L_{II} = 3.3 \times 10^7 M^{-1}$; and $L_I = 3.3 \times 10^4 M^{-1}$.

Partial pressure of CO (mm-Hg)		Concentration ratio p_{CO}^{I}/p_{CO}^{II}
Dark chamber (II)	Illuminated chamber (I)	
7.3×10^{-3}	6.6	900
2.2×10^{-2}	18.4	833
7.35×10^{-2}	36	500
2.2×10^{-1}	55	253
7.35×10^{-1}	66	90
22	79	3.6

Some of the properties of photodiffusion membranes can be deduced from Eq. 1 (*9*). The maximum contribution of differences in light intensity alone to the transport of permeant is given when the concentration of permeant is the same at both boundaries of the film; that is, $[A]_I = [A]_{II} = [A]$. Then the light-induced permeant flux, when there is no concentration difference across the membrane, will be given by

$$N_A = \frac{D_{AB}}{d}[B]_t[A] \times \left[\frac{(L_{II}^{-1} - L_I^{-1})}{(L_I^{-1} + [A])(L_{II}^{-1} + [A])}\right] \quad (2)$$

The optimum concentration of A in both chambers that will show the maximum effect of light on transport is $[A] = 1/(L_I L_{II})^{1/2}$.

The maximum concentrative or pumping effect of light energy is obtained when the photodiffusion flux is balanced by the leakage of free permeant down its concentration gradient; that is, when $N_A = 0$.

Again from Eq. 1 at $N_A = 0$ we obtain

$$[A]_I\left(D_A + \frac{D_{AB}[B]_t}{L_I^{-1} + [A]_I}\right) = [A]_{II}\left(D_A + \frac{D_{AB}[B]_t}{L_{II}^{-1} + [A]_{II}}\right) \quad (3)$$

Some illustrative values of light-induced enrichment ratios calculated for the system myoglobin-CO from the data of Bonaventura *et al.* (*6*) are listed in Table 1. The selective increase in concentration of the photosensitive permeant is astonishing, reaching a maximum ratio of about 900 when the fractional saturation of the carrier with permeant is low; $1 >> L_I[A]_I$ and $1 >> L_{II}[A]_{II}$. Under these conditions we can see the effect of the parameters of the system directly from Eq. 3.

$$\frac{[A]_{II}}{[A]_I} = \frac{D_A + D_B[B]_t L_I}{D_A + D_B[B]_t L_{II}} \quad (4)$$

If, as in the example shown in Table 1, D_A is small relative to the other parameters, then $[A]_I/[A]_{II} = L_{II}/L_I$. The maximum enrichment ratio of permeant is rather independent of all parameters in the system, except for the effect of light intensity as it influences the values of the association constant. The behavior of this system for concentrating permeants is rather unique in that it is more ef-

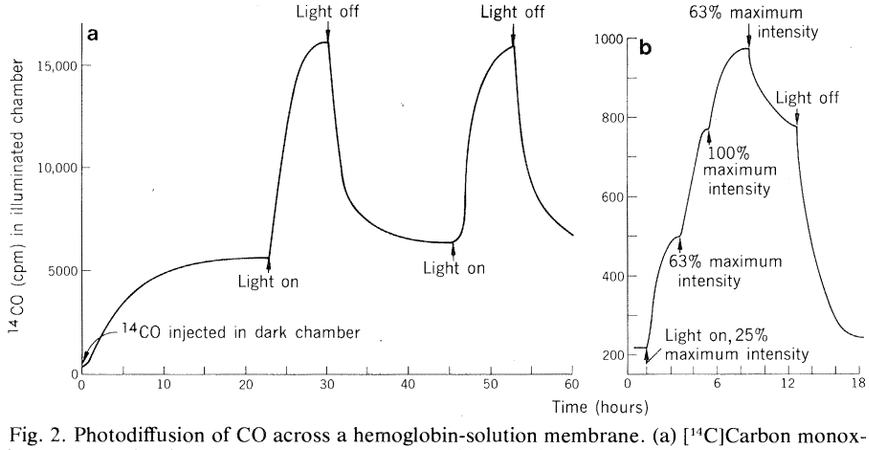

Fig. 2. Photodiffusion of CO across a hemoglobin-solution membrane. (a) [^{14}C]Carbon monoxide accumulation in chamber I first reaches equilibrium with the ^{14}CO content of chamber II. When chamber I is illuminated ^{14}CO accumulates above the initial equilibrium level, and the process is reversible as shown by subsequent cycles. (b) The concentration of ^{14}CO in chamber I is directly related to the light intensity on this side of the membrane. The light intensity was changed by interposing different neutral density filters in the illuminating beam. Experimental conditions: membrane sandwich consisting of two microporous filters (Gelman) separated by a porous silver filter (Selas); diameter, 3 cm; thickness, 0.03 cm; solution, 15 percent human hemoglobin; CO partial pressure in nitrogen, 0.125 mm-Hg; chamber I, 4 ml; chamber II, 20,000 ml. In these experiments the Geiger counter for detection of ^{14}C was placed in a bypass loop of chamber I. The circulation of gas through the bypass was very slow and limited the response of the radiation-detecting system, which accounts for the prolonged periods required to reach steady state. Subsequent experiments with improved circulation showed that steady state is reached in less than 30 minutes. The light source was a 100-watt xenon halide lamp, and the light was passed through a $CuSO_4$ solution to remove heat-producing infrared radiation before it was focused onto the membrane surface. The temperature rise in the membrane due to illumination was less than 1°C, as measured by a thermocouple placed within the membrane sandwich.

fective the lower the concentration of the permeant on the dark side of the membrane.

The concentration difference produced by a photodiffusion membrane system represents potential energy that can be stored in a coupled system or utilized in the form of work; by this mechanism photodiffusion membranes can provide an approach to the capture and utilization of solar energy.

Indirect photodiffusion membranes. Similar effects can be produced with permeants whose binding reactions with the carrier species are not photochromic, provided competing species can be found whose reaction with the carrier is photochemically activated. This is one form of photosensitization. For example, consider the system O_2, CO, and myoglobin. It is known that the quantum efficiency of light for dissociation of carboxyhemoglobin is about 0.4 (*10*), whereas that for dissociation of oxymyoglobin is 100 times lower. However, because both O_2 and CO compete for the same carrier, the light sensitivity of the CO reaction can be used to effect the concentration of O_2 across a photodiffusion membrane. The equation for O_2 transport across a myoglobin (Mb) membrane in the presence of CO under reaction equilibrium conditions is

$$N_{O_2} = \frac{D_{O_2}}{d}([O_2]_I - [O_2]_{II}) + \frac{D_{Mb}}{d}[Mb]_t K\left(\frac{[O_2]_I}{1 + K[O_2]_I + L_I[CO]_I} - \frac{[O_2]_{II}}{1 + K[O_2]_{II} + L_{II}[CO]_{II}}\right) \quad (5)$$

In this case the binding constant, K, for O_2 to myoglobin is the same on both sides of the film, whereas the association constant for CO-myoglobin can be altered by differential illumination. Inspection of Eq. 5 shows that under conditions where $L_I \neq L_{II}$, an O_2 flux across the membrane can be induced even if the ambient concentrations of this nonphotochemically sensitive species are equal on both sides of the membrane. For example, if equal O_2 and CO partial pressures were maintained on both sides of the membrane, the expected concentration profiles that would develop within the membrane are as illustrated in Fig. 2c, and the net flux of O_2 across the membrane would be from the illuminated to the dark side.

We have demonstrated this indirect coupling of O_2 transport to illumination in some preliminary experiments, using hemoglobin as the carrier species. A membrane sandwich (as described in Fig. 2) was placed in contact with an O_2-sensing electrode in a CO-O_2-N_2 gas environment. When one side of the membrane was illuminated, the O_2 electrode indicated an increase in the O_2 concentration on the dark side of the membrane. The effect was reversible.

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References and Notes

1. P. F. Scholander, *Science* **131**, 585 (1960); G. M. Shean and K. Sollner, *Ann. N.Y. Acad. Sci.* **137**, 759 (1966); W. J. Ward and W. L. Robb, *Science* **156**, 1481 (1967); C. Pressman, *Fed. Proc. Fed. Am. Soc. Exp. Biol.* **27**, 1283 (1968).
2. J. S. Schultz, J. D. Goddard, S. R. Suchdeo, *AIChE J.* **20**, 417 (1974); J. D. Goddard, J. S. Schultz, S. R. Suchdeo, *ibid.*, p. 625.
3. D. R. Olander, *ibid.* **6**, 233 (1960); J. D. Goddard, J. S. Schultz, R. J. Bassett, *Chem. Eng. Sci.* **20**, 121 (1965).
4. S. K. Freidlander and K. H. Keller, *Chem. Eng. Sci.* **20**, 121 (1965); R. Blumenthal and A. Katchalsky, *Biochim. Biophys. Acta* **173**, 357 (1969); F. Kreuzer and L. J. C. Hoofd, *Respir. Physiol.* **8**, 380 (1970); K. A. Smith, J. K. Meldon, C. K. Colton, *AIChE J.* **19**, 102 (1973).
5. J. Haldane and J. Lorrain-Smith, *J. Physiol. (London)* **20**, 497 (1895).
6. C. Bonaventura *et al.*, *Biochemistry* **12**, 3424 (1973).
7. M. Mochizuki and R. E. Forster, *Science* **138**, 897 (1962).
8. The experimental evidence shown in Fig. 2 confirms the observations of Mochizuki and Forster (*7*) on the facilitated transport of CO by hemoproteins. J. B. Wittenberg [*J. Biol. Chem.* **241**, 104 (1966)] was unable to demonstrate this effect, and others proposed mathematical analyses to try to prove that CO facilitation could not be obtained in practice [J. D. Murray and J. Wyman, *J. Biol. Chem.* **246**, 5903 (1971); P. Mitchell and J. D. Murray, *Biophysik* **9**, 177 (1973)].
9. The equations in this report are based on simple unimolecular binding behavior. In other cases, the actual equilibrium binding functions should be used. For example, in the CO-hemoglobin system of Fig. 2, the saturation function, Y_{CO} can be represented by the Hill equation (*10*)

$$Y_{CO} = \frac{{p_{CO}}^n}{{p_{50}}^n + {p_{CO}}^n}$$

where p_{CO} is the partial pressure of CO, p_{50} is the partial pressure of CO that gives half saturation, n is the Hill constant, and both n and p_{50} may be functions of light intensity. In this case Eq. 1 becomes

$$N_{CO} = \frac{D_{CO}H_{CO}}{d}(p_{CO_I} - p_{CO_{II}}) + \frac{D_{Hb}4[Hb]_t}{d}(Y_{CO}{}^{I} - Y_{CO}{}^{II})$$

where H_{CO} is the solubility of CO in water.
10. E. Antonini and M. Brunori, *Hemoglobin and Myoglobin in Their Reactions with Ligands* (North-Holland, Amsterdam, 1971).
11. Supported in part by NIH grant GM-15152, Research Career Development Award 1KOGM08271, and the Volkswagen Werke Foundation. The assistance of K. Murai, R. Deno, and M. Flessner in obtaining the data of Fig. 2 is gratefully acknowledged.

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Long Waves in the Eastern Equatorial Pacific Ocean: A View from a Geostationary Satellite

Abstract. *During 1975, westward-moving long waves with a period of about 25 days and a wavelength of 1000 kilometers were observed at a sea surface temperature front in the equatorial Pacific on infrared images obtained by a geostationary environmental satellite system. The absence of these waves during 1976, and the above-average equatorial sea surface temperatures during 1976, may be related to a decrease in the southeasterly trade winds during that year.*

The major components of the current system in the tropical oceans are the alternating bands of eastward- and westward-flowing currents in the surface layers. Although the existence of these currents has been known for a considerable time, very little information is available about their variability. For example, one of the principal results of the multiship experiment conducted in the tropical Atlantic during the summer of 1974 was the discovery that the Atlantic equatorial currents have fluctuations with a period of about 16 days. The phase speed of these oscillations is in a westward direction, and a wavelength of 2500 km has been estimated by Düing *et al.* (*1*). Recent measurements by Harvey and Patzert (*2*) near the ocean floor in the eastern tropical Pacific show current fluctuations that suggest westward-propagating waves with a wavelength of about 1000 km and a period of approximately 25 days. I present here evidence, obtained by a geostationary environmental satellite (*3*), that there are similar westward-propagating long waves in the surface layers of the eastern equatorial Pacific.

The westward flow in the vicinity of the equator is part of the South Equatorial Current. It is associated with low temperatures because of equatorial upwelling and the advection of cold water from the coast of South America. The neighboring current to the north, the eastward North Equatorial Countercurrent, advects relatively warm water from the west. The boundary between these currents is associated with large latitudinal temperature gradients, especially in the eastern Pacific. The gradients are sufficiently large for the associated thermal front (*4*) to be visible on infrared satellite images such as those shown in Fig. 1, a through d. The relatively colder water (lighter shades of