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The Mechanism of a Selective Permeation of Ions through "Solvent Polymeric Membranes"

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Abstract

The mechanism of diffusion of uranyl nitrate in "solvent polymeric membranes" was investigated. It is suggested that a "carrier" transport mechanism is responsible for the selective permeation of ions or ion pairs through such membranes. The fluidity of the membranes was investigated by proton magnetic resonance and by the "fluorescent probe" technique. Radioactive labeling was used in order to determine the self-diffusion coefficient of dicresylbutylphosphate (DCBP) which serves both as plasticizer and as complexing agent in such membranes. Comparison of its value ($\sim 10^{-7}$ cm^2/sec) with the limiting value of the diffusion coefficient of uranyl nitrate in such membranes (3.3×10^{-8} cm^2/sec) indicates that the latter diffuses as a $(DCBP)_2UO_2(NO_3)_2$ complex. It is also suggested that the study of the "solvent polymeric membranes" may help to understand certain properties of biological membranes.

INTRODUCTION

Plasticization of a polymer is a process in which plasticizer molecules neutralize the secondary valence forces between the polymeric chains, thus increasing the mobility of the molecular segments and decreasing the glass transition temperature of the system. Above the glass transition temperature the mobility of plasticizer molecules within the polymeric network may apparently be quite high (*1*). It was suggested (*2*) that

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membranes suitable for ionic separations may be formed if compounds that act both as plasticizers and as selective solvents are used as plasticizing components. Selective permeation of uranyl nitrate was achieved by using various alkyl-aryl phosphates as plasticizers for polyvinyl chloride (*3*, *4*). Indeed, organic phosphates are known to act as effective complexing agents of uranyl ions (*5*). In such membranes, rapid and selective ionic fluxes were observed when the plasticizer content was kept at a 70–80% level. Similar systems based on organic phosphonates were also shown (*6*) to act as effective permeators for ferric and cupric ions. The term "solvent polymeric membranes" was introduced to describe such systems. They are generally composed of a low molecular weight active component contained within a suitable polymeric network. The diffusion coefficients of certain salts and water in such membranes are remarkably high although the very high ionic fluxes observed are also due to changes in their morphology (*7*), which take place under the osmotic gradients and cause a large increase in the effective membrane area.

Two distinct diffusion mechanisms may be considered for such systems, namely: a "site-to-site exchange" or a "carrier transport" mechanism. The former visualizes the movement of the permeating molecule as a series of "jumps" between fixed complexing sites. A "jump" becomes possible when the bond between the complexing site and the permeating ion is momentarily broken. Hence the diffusion coefficient in such a case will be determined by the average lifetime of the complex. On the other hand the "carrier transport" mechanism implies that the complex may move within the membrane as an entity. Thus the diffusion coefficient of the permeating ion will be closely related to the mobility of the complexing plasticizer. A clear understanding of the mechanism involved is obviously essential for the development and improvement of separation processes based on "solvent polymeric membranes." Transport of ions through biological membranes was also discussed (*8*, *9*) in terms of a "carrier" mechanism. Though the distinction between the mechanisms, as previously defined, loses its sharpness for the biological membrane, nevertheless, even in such systems, at least a rotational movement of the complex may be required in order to transfer the permeating ion across a membrane. The elucidation of the ionic transport mechanism in "solvent polymeric membranes" may, therefore, also be of interest for biomembranes. Although such membranes are often treated as ideal bilayers of phospholipids, such treatment seems to be inadequate for the understanding of many experimental findings. For example, high mechanical strength of biological membranes, various degrees of mobility of the

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phospholipidic chains as determined by the spin label or the ^{13}C-NMR techniques (*10*), and the ability of biological membranes to expand without loss of selectivity can not be explained within the framework of such oversimplification.

It seems that the interaction between the polymeric matrix of proteins and the relatively low molecular weight phospholipids must also be taken into account. Our system provides an example of membranes based on such interactions only.

We decided to explore the mechanism of diffusion in "solvent polymeric membranes" by comparing the mobilities of permeating ions on the one hand and of plasticizer molecules on the other. Polyvinyl chloride membranes plasticized with dicresylbutylphosphate were used in this study.

EXPERIMENTAL SECTION

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Materials: Uranyl nitrate, BDH; polyvinyl chloride (PVC) powder, Rhodopas XHP grade C, Rhone-Poulenc; Rhodamine B, Fisher reagent; C-14 labeled butanol, Amersham; phosphoroxychloride, BDH; and cresol, practical grade, Fluka, were used without further purification.

Labeled dicresylbutylphosphate (DCBP)* was synthesized (*11*) by refluxing 1 mole of $POCl_3$ with 2.2 moles of cresol in benzene in the presence of 0.2 *M* $AlCl_3$. The monochloride was distilled in a high vacuum at 10^{-2} Torr. The middle fraction distilling at 135–140°C was collected. The monochloride thus obtained was reacted in the presence of pyridine with labeled butanol in benzene (1.1 mole of butanol per mole of monochloride).

"Solvent polymeric membranes" were prepared as described elsewhere (*7*). The ratio of PVC to DCBP in membranes was 1:3.3. Their mechanical strength was tested with an Instron Universal Tester on 0.8 cm wide and 8 cm long strips. Edges of the test strips were protected with small pieces of Parafilm. The tensile strength at 25°C for a 78% DCBP membrane was 15 ± 1 kg/cm² and its ultimate elongation ~400%. Introduction of 0.1 m*M* of $UO_2(NO_3)_2$ per 1 g of membrane increased its tensile strength to 18 ± 1 kg/cm² and decreased the ultimate elongation to about 300%.

Solutions of uranyl nitrate in DCBP were prepared by stirring crystals of uranyl nitrate in DCBP. After separation of the aqueous layer, the solutions were dried for 48 hr over Drierite and Linde molecular sieves, BDH, Type 4A.

NMR measurements were performed with a Varian A-60 spectrometer on membranes rolled into scrolls 4 cm long and 0.3 cm in diameter.

Fluorescence measurements (for the "fluorescent probe" determinations of the microviscosity) were performed on 100 μ thick membranes containing about 2×10^{-4} mM/g of Rhodamine B and floating in paraffin oil. The technique and the equipment used for these determinations was recently discussed by Shinitzky et al. (*12*).

Diffusion and self-diffusion measurements were performed along membrane strips on plates, and across membranes in dialytic cells. A typical setup for a diffusion experiment on a plate is shown in Fig. 1. A uniformly thick (about 50 μ) membrane (A) is cast on a 10×20 cm glass plate (I). Part of the membrane surface is covered with a 10×15 cm glass plate (II). Membrane B containing labeled DCBP* or uranyl nitrate is cast on a 10×5 cm glass plate (III). Membrane B is placed on Membrane A along the edge of Plate II. The two membranes must adhere tightly with no air pockets left in between. After 48 hr Membrane B is removed and the diffusion of DCBP* or of uranyl nitrate continues across the zero line marked by the edge of Plate II. Though during the first 48 hr the concentration of the diffusing component in Part r of Membrane A—which serves as a reservoir of the diffusiong species—is not rigorously defined, the error introduced by neglecting this in the calculations is small in view of the very long time of the experiment (30–60 days).

Diffusion experiments across membranes were carried out in Perspex dialytic cells. Prior to an experiment, membranes were conditioned by immersion in liquid DCBP. The excess of plasticizer was blotted from the membrane surface with filter paper, and the increase in plasticizer content in the membrane, due to such treatment, was determined gravimetrically. Membranes were mounted between Neoprene O-rings. One compartment of the dialytic cell was filled with about 15 cc of DCBP while the second compartment was filled with 15 cc of labeled DCBP*

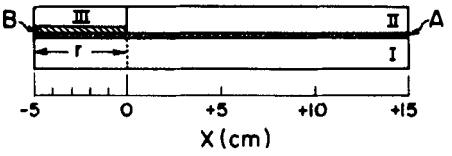

FIG. 1. Experimental set up for the diffusion experiments in membrane strips deposited on glass plates.

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or with 15 cc of uranyl nitrate solution in DCBP. During the diffusion experiment, proper stirring was attained with magnetic stirrers rotating in the centers of the two compartments about 5 mm from the membrane surfaces. At appropriate time intervals 0.2 ml samples were removed with Eppendorf's microliter pipette B 315-E. The radioactivity of the samples was determined with a Packard Scintillation counter. Concentration of uranyl nitrate was checked spectrophotometrically (*13*) with Arsenazo II reagent at 600 mμ after it was extracted with aqueous sodium carbonate from DCBP solutions diluted with hexane. Samples were acidified and evaporated to dryness before analysis.

RESULTS AND DISCUSSION

The conditions for the diffusion and self-diffusion experiments in membrane strips were set up in such a way that at $t = 0$, $C = C_0$ for $X < 0$, and $C = 0$ for $X > 0$ (see Experimental Section) while, at the end of the experiment, the changes in concentration near the boundaries of the test strip were still negligible. Under such conditions the diffusion coefficient may be calculated in a rigorous way (*14*) by determining the total amount of the diffusing species (S) at time t for $X > 0$; viz., $D = S^2\pi/C_0^2t$, where S is the total radioactivity in counts/min at time t in the section of Membrane A extending from $X = 0$ to $X = 5$ cm, and C_0 is the radioactivity for unit length in counts/min cm in the segment of Membrane A extending from $X = -5$ cm to $X = -4$ cm.

A plot of $[S/C_0]^2$ vs. time shown in Fig. 2 yields $D_{25}^{\text{DCBP}} = 7.7 \times 10^{-8}$ cm^2/sec for the self-diffusion of DCBP in a plasticized membrane containing 78% DCBP. Increase in the plasticizer content up to 88% does not, apparently, have a great effect on its mobility since $D_{25}^{\text{DCBP}} = 9.0 \times 10^{-8}$ cm^2/sec is calculated from diffusion experiments conducted across such membranes in dialytic cells (see Fig. 3). On the other hand, the mobility of DCBP was too small to permit reliable determination of the self-diffusion coefficient in membranes in which the plasticizer content was reduced to 50%. This is in agreement with the analysis of the NMR spectra of such membranes. While a line width of 25–50 Hz was observed for the aromatic proton peaks of DCBP in membranes containing 78 and 88% plasticizer (see Fig. 4), no proton peaks could be detected after plasticizer content was reduced to 50%. Apparently the NMR signal vanishes because of a very considerable line broadening due to the restricted mobility of DCBP molecules in such membranes.

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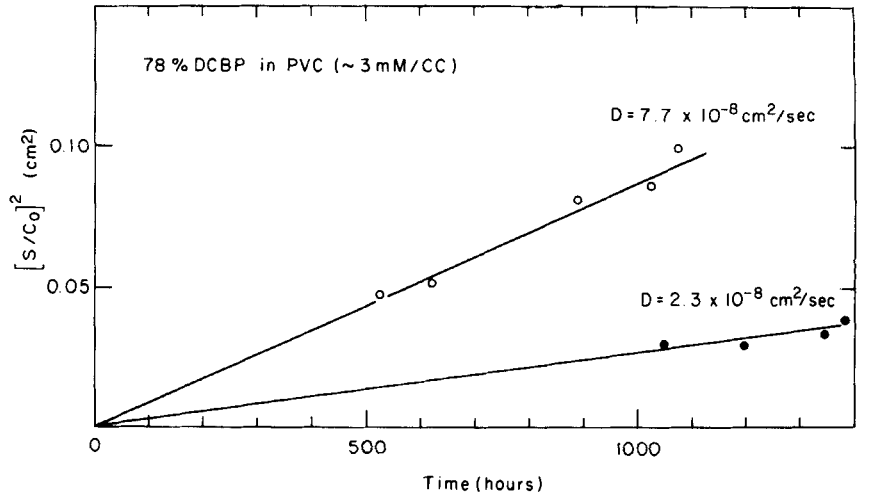

FIG. 2. Self-diffusion of labeled DCBP in membrane strips deposited on glass plates. (○) Membrane containing 78% DCBP, no $(UO_2)(NO_3)_2$. (●) Membrane containing 78% DCBP and 0.7 M $(UO_2)(NO_3)_2$.

The diffusion coefficients for uranyl nitrate in "plasticized" membranes decrease with the increased concentration of uranium in the membrane. As may be seen from data listed in Table 1, the decrease in D^U is inversely proportional to the apparent viscosity of the system. The decrease of $D_{25}{}^{DCBP}$ in the presence of uranyl nitrate is even more pronounced.

Assuming that in such membranes part of the DCBP will diffuse as uranyl complex and that for free DCBP its diffusion coefficient in the presence of uranium may be calculated by using the Walden rule ($D\eta$ = const), one may compare the experimentally determined diffusion coefficient with that predicted on the basis of such assumptions. If two molecules of DCBP complex with one molecule of uranyl nitrate, the fraction of free DCBP in the membrane is about 0.5 [for 0.7 mM/cc concentration of uranyl nitrate, assuming that virtually all $(UO_2)(NO_3)_2$ has been complexed]. Hence, one calculates $D_{app}{}^{DCBP} \sim 2.3 \times 10^{-8}$ cm²/sec, in agreement with the experimentally observed value (see Fig. 2). The comparison of the self-diffusion coefficient of DCBP with the value of the diffusion coefficient of uranyl nitrate in very diluted systems (cf. Table 1) again indicates that uranyl nitrate diffuses in the form of a $(DCBP)_2UO_2(NO_3)_2$ complex.

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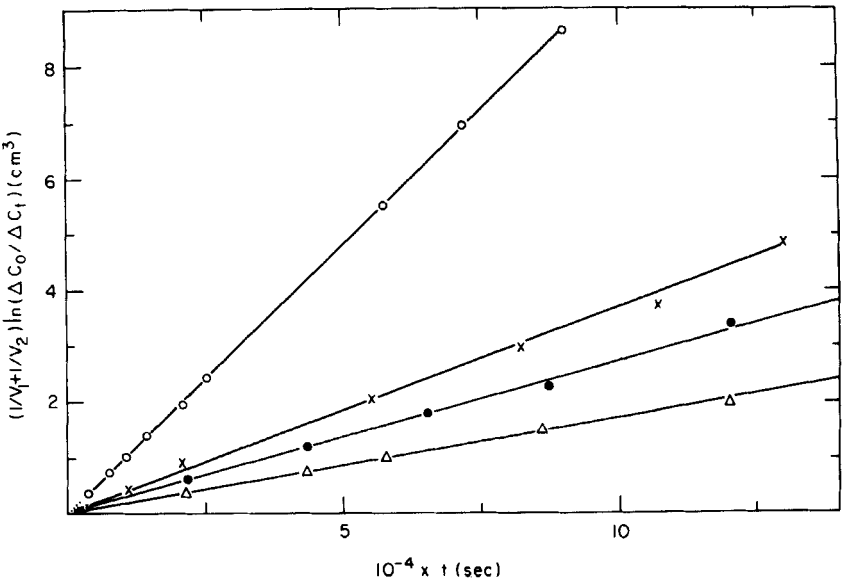

FIG. 3. A typical plot of $(1/v_1 + 1/v_2)$ ln $(\Delta C_0/\Delta C_t)$ vs. time for self-diffusion of DCBP and diffusion of uranyl nitrate across membranes containing 88% of DCBP. (○) Self-diffusion of DCBP, no $(UO_2)(NO_3)_2$. Diffusion of $(UO_2)(NO_3)_2$: (×) 0.015 *M*, (●) 0.12 *M*, (△) 0.7 *M*.

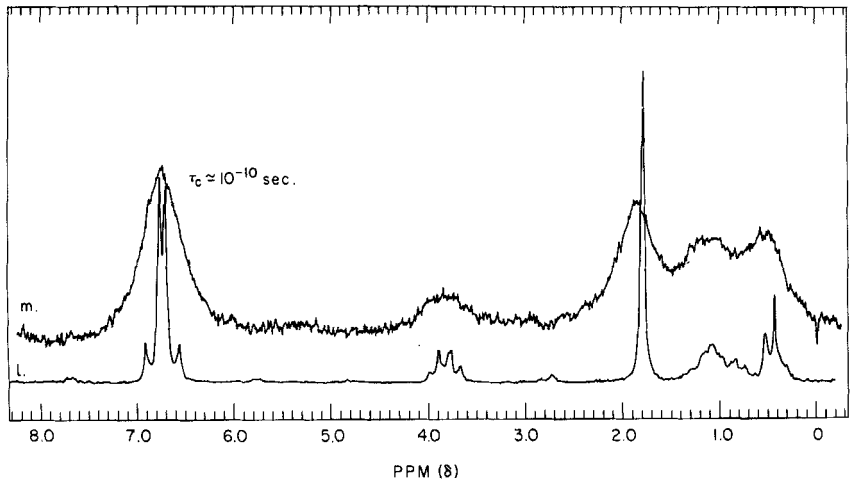

FIG. 4. PMR spectrum of DCBP. m: Membrane containing 78% DCBP. L: Pure DCBP.

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TABLE 1

Diffusion of Uranyl Nitrate and of Dicresylbutylphosphate (DCBP) in PVC Plasticized Membranes at 25°C. Concentration of DCBP in Membranes, 2.9–3.2 mmoles/cc

Concentration of uranyl nitrate in membrane (mmole/cc)	η_{app} in membrane (P)	$D_{DCBP} \times 10^8$ (cm²/sec)	$D_U \times 10^8$ (cm²/sec)	a_{app} [c] (A°)
None	0.465[a]	8.7 ± 1.0	—	5.4
0.015	0.470[a]		3.3 ± 0.3	
0.120	~0.700[b]		2.5 ± 0.2	12.9
0.700	~1.200[b]	2.3 ± 0.2	1.5 ± 0.2	

[a] 2×10^{-4} M concentration of Rhodamine B used as a fluorescent probe.
[b] Calculated from respective viscosities in DCBP solutions.
[c] Calculated for $a_{app} = 2.2 \times 10^{-7}/\eta D$.

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The values of microviscosities within the membrane may be derived from measurements of fluorescence depolarization of Rhodamine B dissolved in such membranes and by comparing it with the fluorescence depolarization of Rhodamine B dissolved in glycerol and in ethylene glycol, viz., a transformation of equations derived by Weber (*15*) yields

$$\eta = [(r_0/r) - 1]V/RT\tau$$

when the molecular anistropy, r, is measured at the wavelength of the excitation beam at which the oscillators of absorption and emission are parallel. η is the viscosity of the medium, T = absolute temperature, R = Boltzman constant, V = effective volume of the fluorescent molecular sphere, and τ = average lifetime of its excited state. $r = I_{\parallel} - I_{\perp}/(I_{\parallel} + 2I_{\perp})$ and r_0 is the value of r when the emitting molecules maintain their orientation excitation and emission, e.g., in very viscous media. $I_{\parallel}$ and $I_{\perp}$ are the fluorescence intensities observed through a polarizer oriented parallel and perpendicular to the plane of polarization of the excitation beam.

The values of τ of excited Rhodamine B molecules were found to be identical (10.8 nsec) for Rhodamine B dissolved in the membrane and in ethylene glycol (see Fig. 5).

Hence

$$\eta_{\text{membrane}} = \eta_{\text{glycol}} \left(\frac{r_0}{r_{\text{membrane}}} - 1 \right) \Big/ \left(\frac{r_0}{r_{\text{glycol}}} - 1 \right) \qquad (1)$$

Values of η_{membrane} were calculated from Eq. (1) assuming $r_0 = r_{\text{glycerol}}$ and by using the plateau values of r's at $\lambda > 520$ mμ for which the limiting polarization is maximal indicating that the oscillators of absorption and emission are parallel (see Fig. 6). Using values of η and D listed in Table 1, one can calculate the molecular radii of the uranyl complex and of DCBP from the Stokes equation $a = kT/6\pi\eta D$ (cf. last row of Table 1). The ratio $a_{\text{complex}}/a_{\text{DCBP}} = 2.4$ is in good agreement with the assumption that the diffusing uranyl nitrate moves together with two DCBP molecules. Absolute values of the calculated molecular radii are, however, too high. The apparent discrepency may be understood if one realizes that rotational diffusion is involved in the "fluorescent probe" measurements while translational diffusion coefficients are measured in our permeation experiments. It is reasonable to expect, indeed, that the polymeric network will hinder more effectively the translational movement of the encapsulated molecules than their rotations.

In conclusion, the results of this investigation strongly support the

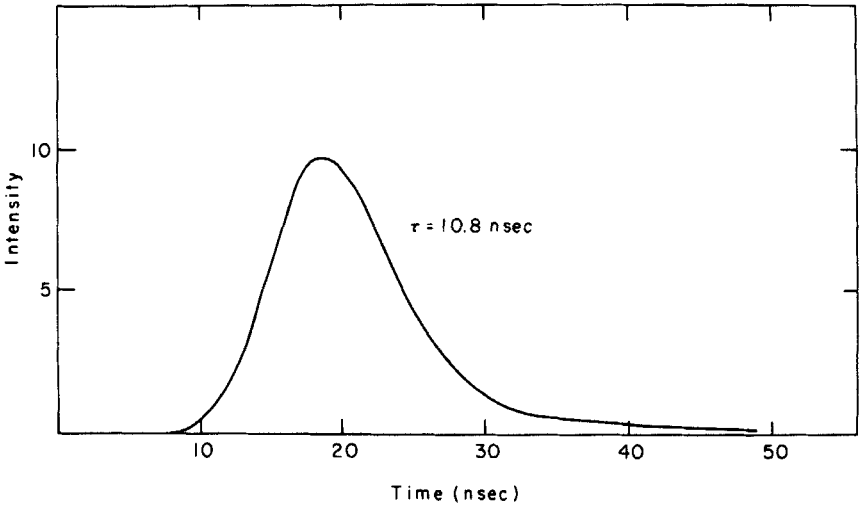

FIG. 5. Lifetime, τ, of excited molecules of Rhodamine B in ethylene glycol solutions and in membranes containing 78% DCBP.

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assumption that a "carrier" transport mechanism is involved in the diffusion of uranyl nitrate through DCBP plasticized membranes. Such a conclusion is also supported by the kinetic results of Weiss and Egozy (*16*), who found that in toluene and CCl_4 solutions at room temperature the rate constant of decomplexation of the DCBP-uranyl nitrate complex, k_d, is of the order of 6×10^3 sec^{-1}. Eyring's treatment of diffusion may be used for the calculation of the diffusion coefficients if a "jump"

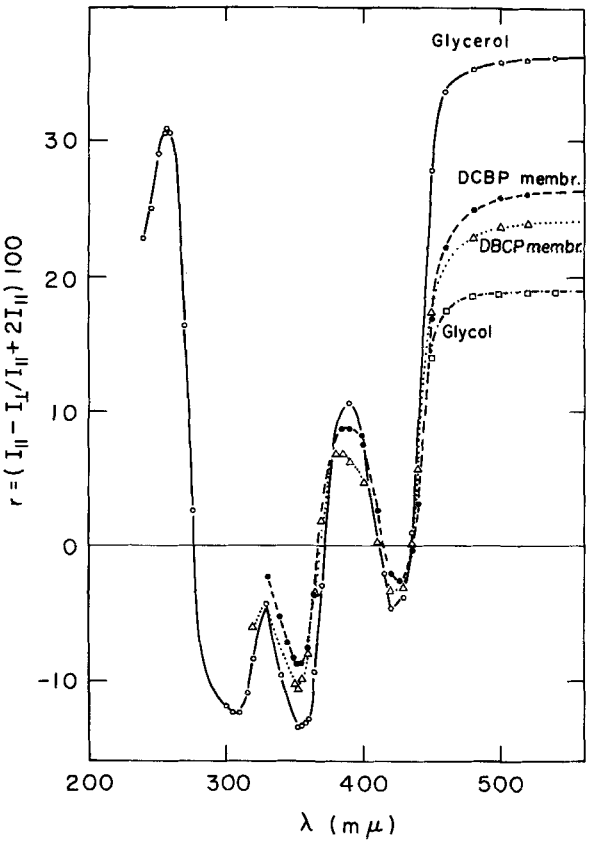

FIG. 6. Fluorescence depolarization of Rhodamine B dissolved in membranes in glycerol and in ethylene glycol. (○) 2×10^{-6} *M* solution of Rhodamine B in glycerol. (●) 2×10^{-4} *M* solutions of Rhodamine B in membranes containing 78–88% DCBP. (△) 2×10^{-4} *M* solutions of Rhodamine B in membranes containing 78% of dibutyl cresyl phosphate. (□) 2×10^{-6} solution of Rhodamine B in ethylene glycol.

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mechanism of diffusion is postulated, viz., $D = \lambda^2 k$. Eyring's rate constant of diffusion, k, may be identified with the decomplexation rate, k_d, and the average distance between active sites, λ, may be estimated from the DCBP concentration in the membrane as $\sim$8 Å. Hence, one calculates $D \sim 10^{-11}$ cm^2/sec. This value is several orders of magnitude smaller than the actually measured values of diffusion coefficients in plasticized membranes. On the other hand, such low values of the diffusion coefficients of uranyl nitrate were indeed recently observed in our laboratory (*17*) for the polymer analogs of the plasticized membranes in which the active phosphatic groups were fixed within the polymeric matrix while a noncomplexing plasticizer was used for plasticization of the membrane. Details of these latter measurements will be reported elsewhere.

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