

Occurrence of Negative Time Lags in Permeability Studies of Solutes through Polyethylene

Keyphrases □ Permeability of solutes through polyethylene—occurrence of lag times □ Polyethylene films—permeability, occurrence of lag times

Sir:

Recently, Serota *et al.* (1) reported their study on the permeability of substituted anilines from aqueous solutions through polyethylene and noted the occurrence of negative time lags. They used the permeation cell according to Rodell *et al.* (2) and determined the permeation rate spectrophotometrically.

Treating the time lag method mathematically, Siegel and Coughlin (3) found that considerable errors could result if the straight line were drawn through data taken after times less than 2θ . By neglecting this fact, smaller values will be obtained, but negative time lags can never result.

In our investigation of the permeability of some phenols and aromatic amines through low density polyethylene, we obtained diffusion coefficients in the 10^{-9} – 10^{-10} cm.² sec.⁻¹ range. For example, in the case of *o*-phenylenediamine, we found a time lag of 130 min., corresponding to a diffusion coefficient of 2.0×10^{-10} cm.² sec.⁻¹ (temperature 35°; film thickness 30.6 μ m.). Therefore, we drew a straight line through data taken after 5 hr. These data are in good agreement with literature values (4).

Using aqueous solutions in a slightly modified cell, we obtained negative time lags if quantitation was done spectrophotometrically in the UV region. Since it is impossible that a considerable amount of substance has permeated at time zero, these data can only be ex-

plained by an anomalous behavior at the beginning of the permeation process. Using a colorimetric procedure (5), however, we obtained the reported results.

We suggest, therefore, that some substance could be eluted from the polyethylene film which shows strong UV absorption. In our experiments, we used polyethylene films¹ without pretreatment. They did not contain additives. To confirm our suggestions concerning the presence of an interfering substance, we extracted the solution in which quantitation was done with chloroform. After evaporation of the organic solvent, we examined the extract by TLC on silica gel [solvent of benzene–petroleum ether (7:3)] by comparison with blank tests. Because of the decomposition of *o*-phenylenediamine during evaporation, the chromatogram could not be evaluated exactly. With phenol as the permeant, however, the starting point of the chloroform extract only gave a green fluorescence. After spraying with 2,6-dichloroquinonchlorimide, only phenol appeared as a colored spot. The green fluorescing spot did not react. Phenol and all other substances were tested for purity by TLC.

After elution from the thin-layer plate, we recorded the UV spectrum of this substance (Fig. 1). It showed considerable absorption and, thus, interfered with the spectrophotometric determination of aromatic compounds. We have not been able to characterize this substance further because of the minute amounts.

If one wishes to interpret this effect, one must assume that elution of this substance occurs at the beginning of the permeation process within a relatively short time. It is due to the interaction between permeant and polymer membrane. Treating the membrane only with water, alcohol, and alcohol–water (1:1), we could not find this substance.

These findings explain the occurrence of negative lag times in the case of compounds with low permeability coefficients if the permeation rate is determined spectrophotometrically. In the investigation of substances with higher permeabilities, experimental lag times may still be slightly positive. The detailed results of our investigations will be published later.

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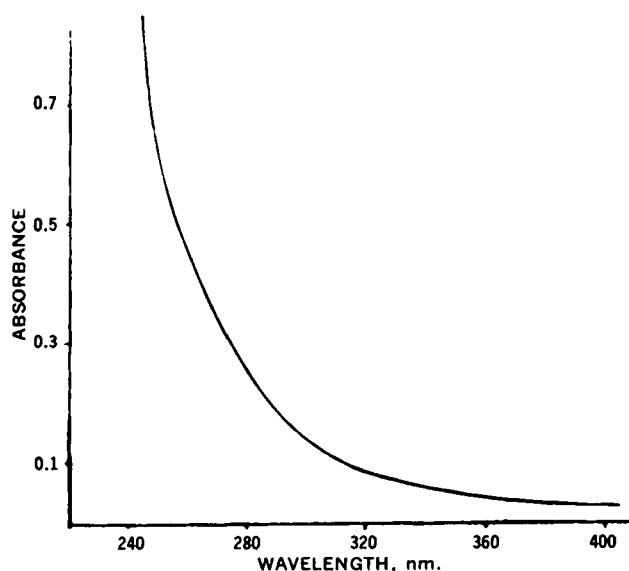


Figure 1—UV absorption spectrum of the unknown substance eluted from polyethylene films.

¹ Mirathen 1310.