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DIFFUSION AND SWELLING STUDIES OF ETHANOL AND ETHYL LAURATE WITH DRY POLYPROPYLENE AND POLYETHYLENE TEREPHTHALATE FILMS USING A RADIOTRACER TECHNIQUE

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Abstract—The diffusion of ethyl laurate and of ethanol through oriented polypropylene and polyethylene terephthalate films has been studied using a new radiotracer method. In dry film experiments, the effect of the swelling process was dominant, determining the apparent diffusion coefficient (D); the latter increased with time because of the swelling effect. The swelling process also determined the magnitude of the time for diffusant first to appear on the opposite side of the film. In concentration gradient experiments, the value of D depended mainly on the average of the concentrations of the swelling agent, ethyl laurate, on both sides of the film; the value of the concentration of ethyl laurate on the radiolabelled side of the film caused a much smaller effect. When swelling agent was present on only one side of the film, the value of D dropped dramatically.

INTRODUCTION

As the polymer industry has developed, studies of the migration of small molecules through polymer materials have become increasingly important. The radiotracer technique has been used for some of these studies, such as of the diffusion of plasticizers [1, 2] and of stabilizers [3–6] in polymers.

In the food packaging industry, a knowledge of the permeability of plastics to small molecules (both compounds which are present in packaging materials and in food) is critical for the quality assurance of food and for consumer protection [7]. Because many of the food products and additives in plastics are in the liquid state, a radiotracer technique with high sensitivity for use under these conditions is required. Such a method has already been reported [8].

A study of the diffusion of ethyl laurate and of ethanol through oriented polypropylene (PP) and polyethylene terephthalate (PET) films using radiotracer techniques is now reported.

EXPERIMENTAL PROCEDURES

The design and general use of the diffusion apparatus have already been described, as have the preparations of [1-^{14}C]ethanol and [1-^{14}C]ethyl laurate [8].

The diffusion of labelled ethanol and of labelled ethyl laurate was investigated through films of either PP (thickness 20 μm) or PET (thickness 12 μm). The films were not allowed to contact any solvent before use, thus maintaining their dry character.

Experiments were carried out at 20° using various mixtures of ethanol and ethyl laurate; the concentrations of components, which were not always identical on both sides of the film, were measured by volume percentage. The amount of activity diffusing through the film was measured by extracting a 1 cm^3 sample from the initially inactive side of the film. The sample was added to 10 cm^3 of a solution of butyl PBD in scintillation grade toluene (15 g dm^{-3}) in a counting vial; it was then counted using an LKB Wallac "Spectral" 1219 Liquid Scintillation Counter. Corrections for self-quenching were made using the calibrated shift in the external standard spectrum for each sample.

Immediately after the removal of each sample for monitoring of radioactivity, an equal volume of unlabelled mixture of the same chemical composition was added to restore the level of the liquid.

Assessments of swelling of films were made by measuring their weights before and after soaking in a given solvent for a defined time.

RESULTS AND DISCUSSION

1. Differences in diffusion between swelling and non-swelling agents

A qualitative comparison of the swelling and diffusion properties of various combinations of compounds and films is given in Table 1. Observations for these preliminary experiments were restricted to a duration of 7 days.

From Table 1, it is clear that diffusion occurs only when at least one swelling agent is present; no observed swelling resulted in no observation of diffusion. But a non-swelling agent (or a very weak swelling agent) can diffuse through a polymer film with the assistance of a swelling agent. It can also be seen that ethyl laurate cannot diffuse through PET film in the presence of ethyl acetate (a swelling agent to PET) whereas ethanol can. The reason may be that the molecular size of the ethyl laurate is much greater than that of the swelling agent, and that sites exposed by swelling are not large enough to allow the penetration of molecules of ethyl laurate.

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Table 1. Diffusion and swelling of PP and PET films observed in various liquids

Compound	PP		PET	
	Swelling	Diffusion	Swelling	Diffusion
Ethanol	No	No	No	No
Ethyl laurate	Yes	Yes	No	No
Ethyl acetate	Yes	—	Yes	—
Ethanol (in ethyl laurate)	—	Yes	—	No
Ethyl laurate (in ethyl acetate)	—	—	—	No
Ethanol (in ethyl acetate)	—	—	—	Yes

2. Effect of swelling during diffusion process

In experiments with dry films, the diffusion processes are clearly complicated. Swelling and diffusion occur simultaneously resulting in plots of amount of diffusion against time being non-linear in the initial stages, as observed in Fig. 1. This figure shows a plot of diffused mass percentage (M), already defined [8], against time for the diffusion of 100% ethyl laurate through PP film.

As swelling continued, the free volume of polymer increased and the exposed sites of free volume permitted diffusion at a higher rate. So the diffusion rate, given by the gradient of the curve, increased with time. The diffusion coefficient (D), derived from these experiments and calculated by the method already reported [8], was the so-called "apparent diffusion coefficient", being affected by the swelling process.

3. Concentration dependence of D in zero concentration gradient

Figure 2 shows plots of M against time for the diffusion of ethanol through dry PP film when the diffusant was mixed with ethyl laurate in various proportions; Fig. 3 shows similar plots when ethyl laurate was the diffusant in the presence of ethanol.

It can be seen that diffusion coefficients were strong functions of concentration; this kind of behaviour has been reported for other systems [9, 10]. Numerous examples in the literature indicate that diffusion processes in polymeric systems sometimes do not follow the laws of classical molecular diffusion. Such non-Fickian diffusion behaviour may be caused by swelling.

As will be shown in a further paper [11], the values of D for pure diffusion of ethanol or of ethyl laurate all decreased as the concentration increased. It is therefore not difficult to explain the dry film behaviour in Figs 2 and 3. For ethanol diffusion (Fig. 2), the increase in ethanol concentration is accompanied by a decrease in ethyl laurate concentration. As the swelling would be slower in smaller concentrations of ethyl laurate, when the concentration of ethanol is increased, the pure diffusion coefficient and the swelling rate decrease simultaneously; thus the apparent diffusion coefficient measured in these experiments decreases.

Figures 2 and 3 also show that the induction time, which is the time for diffusant first to appear on the inactive side of the film, also depended on the concentration of the swelling agent and therefore on the swelling rate. The larger the concentration of the swelling agent, the shorter was the observed induction time.

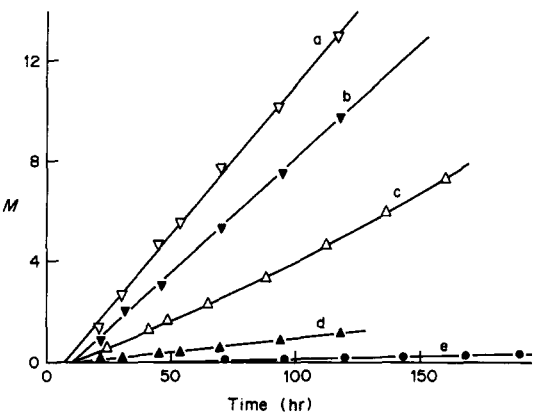

Fig. 2. Effect of concentration of ethanol (in ethyl laurate) on plots of M against time for its diffusion through dry PP film; concentrations of ethanol by volume: (a) 3.5% (b) 7% (c) 14% (d) 50% (e) 75%.

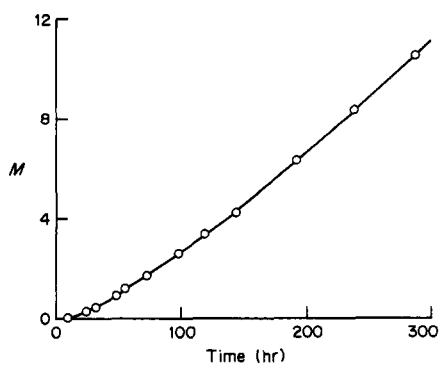

Fig. 1. Plot of M against time for diffusion of 100% ethyl laurate through dry PP film.

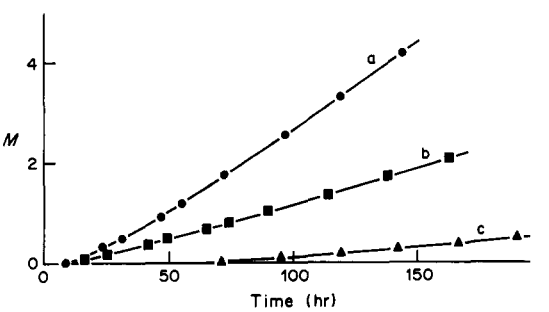

Fig. 3. Effect of concentration of ethyl laurate on plots of M against time for its diffusion through dry PP film; concentrations of ethyl laurate by volume: (a) 100% (b) 50% (c) 25%.

Table 2. Relationship between concentration of swelling agent and D

Conc. of ethyl laurate in active chamber	Conc. of ethyl laurate in inactive chamber	Mean conc.	$D(10^{-11}\,cm^2\,sec^{-1})$
100	100	100	15.1
50	100	75	11.9
75	75	75	10.5
100	50	75	9.3
7	100	53.5	7.9
25	75	50	7.7
50	50	50	7.3
100	7	53.5	6.7
100	0	50	4.6
10	40	25	4.1
25	25	25	2.2
40	10	25	1.9
50	0	25	1.4

For the diffusion of ethyl laurate (Fig. 3), the pure diffusion coefficient and the swelling rate change in opposite directions. When the concentration of ethyl laurate increases, the real diffusion coefficient would be decreased, but the swelling rate would be increased. The net result was a dramatic increase in the apparent diffusion coefficient. This shows that the effect of swelling under such circumstances was dominant.

4. Concentration dependence of D in a concentration gradient

In order to understand better the effect of swelling, some concentration gradient experiments were carried out, comparing them with zero concentration gradient experiments; the results are summarized in Table 2. It is of interest to note that the apparent diffusion coefficients of ethyl laurate appeared to depend mainly on the average of the concentrations of the swelling agent (ethyl laurate) on both sides of the film. Although the plots from which these data are derived are gently curved, there was no difficulty in most cases in determining the initial gradients to calculate D. The linearity of plots was also affected by the average concentration of the swelling agent, the plots for higher concentrations being more curved over the time scale used.

The results in Table 2 show further domination of swelling in diffusion through dry PP films. The effect of concentration gradient and hydrostatic head, resulting from the different densities, clearly played a less important role in these processes.

It can also be seen in Table 2 that D decreased slightly when the concentration of ethyl laurate in the active chamber increased. This decrease was consistent with the fact that the real diffusion coefficient decreased with increase in the concentration of ethyl laurate, an observation which will also be published elsewhere [11].

When the concentration of swelling agent in the inactive side was 0%, D become smaller. This decrease may arise because the speed of swelling from two sides was much greater than that from only one side, although the average of the concentrations on both sides of the film was the same.

CONCLUSIONS

The modified radiotracer technique is highly effective for measuring small amounts of diffusion through polymer films. It can be used to obtain the apparent diffusion coefficients for dry film under conditions of zero and finite concentration gradient.

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