# Fluorescence measurements of the diffusion coefficient for butylated hydroxyanisole in low-density polyethylene

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Measurement of the diffusion coefficient ($D$) of butylated hydroxyanisole (BHA) in low density polyethylene at 31°C was made by two techniques. (1) Measurement of diffusion rate in the absence of solvent was made by use of a film stack with BHA-loaded discs on top and bottom. After a given diffusion time, the films were separated and the BHA extracted from the films into 1-propanol. The fluorescence of the solutions provided values of BHA concentration as a function of film position in the stack, from which the value 3.4 (SD 0.3) $\times 10^{-9}$ cm$^2$ s$^{-1}$ for $D$ was calculated. (2) Fluorescence monitoring, under oxygen free conditions, was used to measure rate of BHA extraction from a film into 1-propanol at 31°C, and gave the value 3.8 $\times 10^{-9}$ cm$^2$ s$^{-1}$ for $D$ which agrees well with the value determined by measurement in the absence of solvent.

## INTRODUCTION

Diffusion coefficient measurements for protective additives through polymers provide information about the length of time the additive will protect a polymeric material. Such knowledge is essential for development of more durable polymer products.

Migration rates of additives from polymers into solvents can be accurately measured by a number of trace analysis techniques. For example, Wang and Howell[1] used a fluorescence technique to measure the migration rate of an antioxidant $N,N'$-diphenyl-$p$-phenylenediamine from low-density polyethylene (LDPE) into 1-propanol. Chang, Pummer and Maurey[2] used a radiotracer technique to measure the migration rates of $n$-$C_{18}H_{38}$, $n$-$C_{32}H_{66}$ and 2,6-bis(1,1-dimethylethyl)-4-methylphenol (BHT) from both high-density and low-density polyethylenes into ethanol and n-octanol at 30 and 60°C.

However, accurate measurement of diffusion coefficients in the absence of solvent has proven difficult. Roe, et al.[3] employed a stack of polyethylene films through which they measured migration rate. After a suitable time interval these investigators separated the films and determined the amount of antioxidant present in each by a thermogravimetric technique based upon the ability of the antioxidant to suppress initiation of an oxidation reaction. The diffusion coefficient was determined from the concentration profile of the antioxidant.

Roe et al.[3] examined the possibility that gaps may exist between the films which offer a resistance to diffusion of the additives. A control experiment with a modified stack of films gave the same result as the regular experiment. Roe et al.[3] concluded that either no gaps exist between the films, or that the antioxidant is transported readily through the vapour phase across the gaps when the gaps exist. Because the additive we used, BHA, is volatile, we believe that any gaps that exist between the films will not significantly affect the diffusion of the BHA and produce significant experimental error.

We measured the diffusion coefficient of butylated hydroxyanisole (BHA) in LDPE in 1-propanol by the method of Wang and Howell and in the absence of solvent by a modification of the method of Roe et al.[3] in which fluorescence detection of the antioxidant replaces the thermogravimetric analysis.

## EXPERIMENTAL*

BHA, purum was purified by producing a saturated solution in warm cyclohexane. The solution was placed in a refrigerator at 4°C for three days. BHA crystals were separated from solvent by filtration on a fritted glass filter when nitrogen pressure was applied to force the liquid through. White, needle-shaped crystals (MP 61°C–62°C remained on the filter. These were dried *in vacuo* and stored under nitrogen until used.

Densities were determined for the LDPE discs used for the film stack experiments, and for the LDPE film used for the extraction experiment from buoyancy measurements when films were immersed in 1-propanol. For this purpose samples weighing approximately 35 mg were first weighed in air. The samples were then immersed in 1-propanol, the system was evacuated to remove any trapped gas bubbles, and the sample was reweighed. The temperature of the 1-propanol was measured to the nearest tenth of a degree.

*Film stack diffusion experiment*

LDPE discs (3.8 cm in diameter) were cut from a 0.01 cm thick sheet of polyethylene film. 100–200 discs

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* In this report, to describe procedures adequately, we have occasionally identified commercial products and equipment. In no case does such identification imply NBS recommendation or endorsement, nor does it imply that the item identified is necessarily the best available for the purpose.

were placed in a 2 l flask to which 1 l of high purity 1-propanol was added. The mixture was stirred for several days to wash the films. Fluorescence of the 1-propanol was measured (excitation at 295 nm, emission at 332 nm) to monitor the presence of leachable impurities which would interfere with BHA determination by fluorometry. If the fluorescence of the propanol washing was higher than that of the original solvent, the washing liquid was decanted from the films, fresh solvent was added, and the stirring process was repeated. Then two porous teflon discs, 3.8 cm in diameter, were washed with ethanol and dried. They were loaded with BHA by the following procedure: the discs were placed in a vessel containing several grams of BHA, and the BHA was melted by immersing the bottom of the vessel in a heated oil bath. The oil bath was removed and the vessel was taken off the vacuum line and tipped back and forth so as to thoroughly impregnate the teflon discs with melted BHA. Then 21 of the LDPE discs were placed between the teflon discs and clamped in a vice. The vice jaws were tightened uniformly as determined by a caliper. The vice and films were put in an oven maintained at 31°C and flushed with nitrogen for an accurately known time interval (approximately two days). The vice was removed from the oven, the teflon discs removed, and the vice again tightened as before to measure the thickness, $2l$, of the films. Then discs 1.9 cm in diameter were cut from the centre of the stack with an arch punch and the outsides discarded to eliminate edge effects. The top and bottom films were also discarded because they may have picked up BHA from contact with the teflon discs. The remaining films were placed in tared vials (one film per vial) which then were reweighed. Extraction of BHA was done by one of the two following methods:

*1. Film stack diffusion–δ extraction in vials.* For this procedure, 10 ml of 1-propanol was added to each film-containing vial. Vial caps were screwed on securely and the vials were shaken gently for 48 h, then reweighed to provide values for the amount of propanol in each vial. Front face fluorescence intensity of the resulting solutions was measured on a fluorometer, employing an excitation wavelength of 295 nm and an emission wavelength of 332 nm. Fluorescence readings were referenced to a quinine sulphate solution (National Bureau of Standards Standard Reference Material 936) excited at 350 nm and emitting at 450 nm.

*2. Film stack diffusion–δ extraction in degassed solutions.* Ten ml of 1-propanol was added to each of six tared vessels containing magnetic stirring bars, of a special type from which it is possible to exclude oxygen during extraction and fluorescence measurements[1]. To provide blank values the vessels containing propanol were attached to a vacuum line, and the propanol was degassed by repeated freezing, pumping and thawing. The vessels were removed from the line and the propanol fluorescence (excitation 295 nm, emission 332 nm) was measured and referenced to a quinine sulphate standard. After re-attachment of the vessels to the vacuum line, one film taken from the stack after diffusion had occurred and then weighed, was added to each vessel under nitrogen. Vessels were removed from the line and stirred magnetically for two days to allow extraction to occur. Then the fluorescence was read on the fluorometer and referenced to the quinine sulphate standard. Since only six films could be

chosen for fluorescence measurement, film choice was important.

For extraction in vials, each fluorescence value (including the solvent blank) was divided by the reading of the quinine sulphate reference solution. A blank value was subtracted from each fluorescence value for an extracted film, and each reading was divided by the grams of film per gram of solvent. The diffusion coefficient of BHA in LDPE was determined by comparing these values with the theoretical plots shown in *Figure 1* of $x/l$ versus relative concentration of the migrant on a logarithmic scale. Curves were calculated and plotted for many values of the dimensionless parameter $K = tD/l^2$ where $t$ is the time of diffusion. Because the measured fluorescence is proportional to the concentration of BHA in the film, the experimental points were shifted horizontally until they matched a theoretical curve, as shown in *Figure 1*. Then the diffusion coefficient is calculated from the $K$ of the theoretical curve.
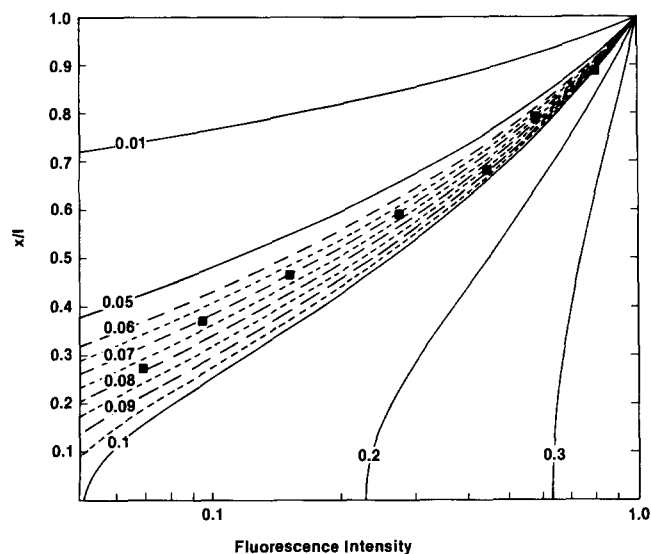


**Figure 1a** Plot of relative distance $(x/l)$ from the center of a film stack as a function of log relative fluorescence read on solutions of BHA produced by leaching films from the stack in 1-propanol without degassing in vials. Lines are theoretical values for values of $K = tD/l^2$
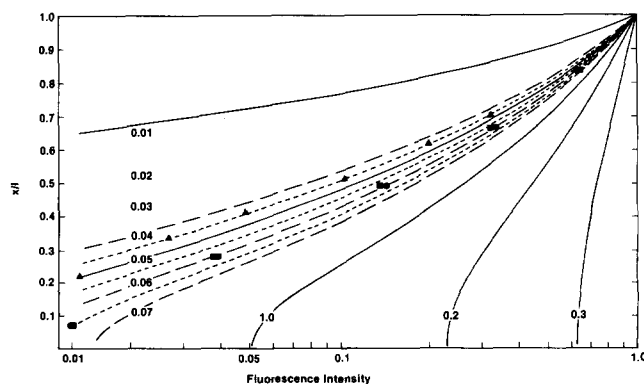


**Figure 1b** Results of two experiments plotted similarly to **Figure 1a** except that measurements were made on films from the upper half of the stack extracted under oxygen-free conditions in vessels from which oxygen was excluded[1]. Values on same samples after (■) 44 and (●) 50 h extraction in 1-propanol. Upper points (▲) obtained from separate experiment; film stack heated for less time

## *Extraction experiment*

Low-density polyethylene samples for extraction measurements were prepared from the National Bureau of Standards Standard Reference Material 1476 whole polymer as described previously[1]. The LDPE was prepared in 0.95 cm diameter films of thickness 0.035 cm. The film stack was placed between two washed LDPE film liners and clamped between two porous teflon discs loaded with BHA as previously described and placed in an oven flushed with nitrogen at 31°C for 48 h. The BHA impregnated film was then put into a special vessel containing 10 ml of degassed 1-propanol in which extraction occurred under oxygen-free conditions as described previously[1]. The fluorescence intensity of the 1-propanol was measured and is plotted *versus* the square root of the time of extraction in *Figure 2*. Values of the diffusion coefficient were calculated by use of the relation:

$$M_t/M_\infty = (4/\pi^{1/2})(Dt/l^2)^{1/2}$$

valid for small times (for which $l$ is the thickness of polymer film undergoing extraction, $t$ is the time in seconds, and $M_t$ and $M_\infty$ are the amounts of diffusing substance present in the extracting solvent at times $t$ and at equilibrium, respectively). Calculation of $D$ was possible if the ratio $M_t/M_\infty$ was replaced by the ratio of sample fluorescence intensity at time $t$, $F_t$, to sample fluorescence intensity after extraction was complete, $F_\infty$. We verified that in the concentration range of these experiments, fluorescence intensity is linearly related to concentration.

## RESULTS AND DISCUSSION

The average value found for the diffusion coefficient from the three measurements made in the absence of solvent by the film stack experiment is $3.4 \times 10^{-9}$ cm² s⁻¹ with a standard deviation of $0.3 \times 10^{-9}$ cm² s⁻¹. Plots of the three data sets appear in *Figures 1a* and *1b*, and numerical values are shown in *Table 1*. This value is very close to the value $3.8$ ($\pm 0.2$) $\times 10^{-9}$ cm² s⁻¹ found with the liquid extraction method by use of the data plotted in *Figure 2*. The density of the film used for the stack was found to be $0.912$ g m⁻¹; that for the extracted film was $0.927$ g ml⁻¹. The closeness of the density values for the two polyethylenes suggests similar degrees of crystallinity for the two samples. This is an important consideration since diffusion is believed to occur only through the amorphous region of the polymer.

The agreement of values found for the diffusion coefficient when measurements were made without solvent with those found by extraction into liquid is considered significant since measurement of $D$ by extraction rate into solvent is much simpler experimentally. By extraction, a value for the diffusion coefficient can be found by making successive measurements on a single degassed solution, whereas six or more are required for determinations made with the film stack.

In *Figure 1b* the lower pairs of points represent two sets of fluorescence values measured on the same samples after 44 and 50 h of extraction in 1-propanol. These points show that extraction is essentially complete after 44 h, and provide an indication of the precision of the fluorescence measurements. The upper points were obtained from a separate experiment for which the film stack was heated a few hours less and therefore yields a different value for $K$.

When vials were used for extraction of films from the stack, extraction of BHA could be done on all but the outermost films, which were not used because of possible contamination with BHA from the teflon discs. With the vials it was possible to obtain more data points than on degassed solutions since all the films from the stack could be extracted simultaneously. However, as can be seen from examination of the data for degassed samples (*Figure 1b*) better precision was obtained when fluorescence determination of BHA was made on these than on samples not degassed (*Figure 1a*). This is mainly because of the insufficient control of the concentration of oxygen which quenches the fluorescence of BHA; the ratio of the fluorescence intensities of BHA in oxygen-free 1-propanol and in oxygen-saturated 1-propanol is 1.22. If all the samples are oxygen-saturated, the effect of oxygen is to reduce the fluorescence by about 22%. This will displace the $x/l$ *versus* log fluorescence plots to the left without producing an error in the value found for $K$ or calculated for diffusion coefficient. In practice, however, the degassed solutions gave much better precision.

It is interesting to compare the value we find for $D$ with BHA ($3.36 \times 10^{-9}$ cm² s⁻¹) at 31°C with the value found
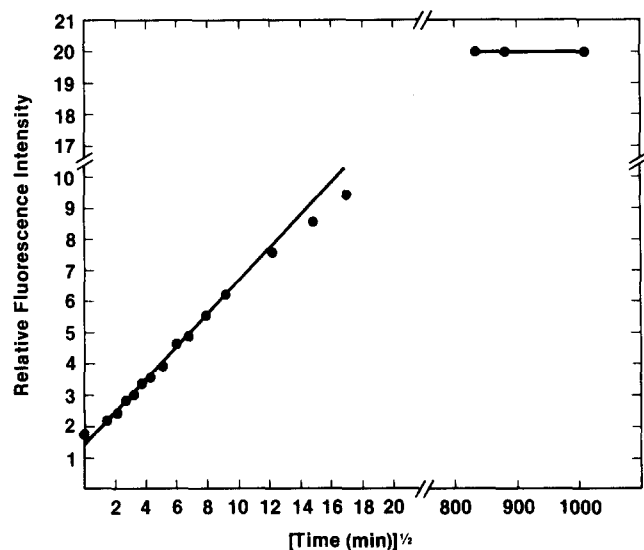


**Figure 2** Plot of fluorescence intensity as a function of square root of time for determination of the diffusion coefficient by extraction rate of BHA from a low density polyethylene film into 1-propanol at 31°C

Table 1  Diffusion parameters for butylated hydroxlyanisole in the absence of solvent

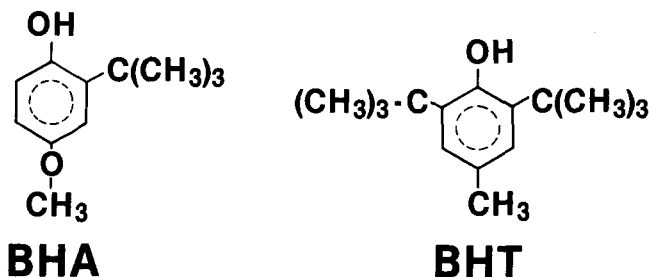| Trial No. | Degassed | Diffusion time $(s \times 10^{-5})$ | $K$ | $D$ (cm² s⁻¹ $\times 10^9$) |
|---|---|---|---|---|
| 1 | No | 1.925 | 0.065 | 3.3 |
| 2 | Yes | 1.729 | 0.06 | 3.7 |
| 3 | Yes | 1.712 | 0.045 | 3.1 |

**Figure 3** Structures of BHA and BHT

by Chang et al.[2] for BHT at 30°C ($0.29 \times 10^{-9}$ cm$^2$ s$^{-1}$). Structures of the two compounds are shown in *Figure 3*. Since the compounds are otherwise very similar, the additional $t$-butyl group of BHT apparently greatly impedes the motion of this molecule through low density polyethylene.

## CONCLUSION

It is possible to find a value for the diffusion coefficient with a standard deviation of 10% by measurement of diffusion rate in the absence of solvent. Measurement of the diffusion coefficient by extraction rate into liquid can be

made with a standard deviation of approximately 2%[1]. For 1-propanol which, like ethanol[6], is expected to be absorbed negligibly by LDPE, the values for the diffusion coefficient of BHA in LDPE obtained by use of the two methods agree well. Therefore the extraction technique, which is experimentally much simpler as well as more precise, may provide a valid measure of diffusion coefficient in low density polyethylene if (1) the solvent is not absorbed by the polymer and (2) the diffusion coefficient does not depend on the migrant concentration. It is of interest to note that BHT has a diffusion coefficient one-tenth as large as BHA under similar experimental conditions.

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