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Effect of Migrant Size on Diffusion in Dry and Hydrated Polyamide 6

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Food safety authorities have already allowed the use of mathematical models to predict diffusion from plastic food contact materials. These models use the molecular weight of the migrant as a cornerstone parameter that describes the contribution of the migrant to the diffusion process. In this work, the dependence of the diffusion coefficient on the migrant size was examined through fluorescence recovery after photobleaching (FRAP). A model migrant series of fluorescent probes was used, covering a wide molecular weight range. The advantage and originality of the tested migrant series are associated with the fact that the same shape and chemical functionality are maintained regardless of the molecular weight of the migrants. In this way the dependence of the acquired data on parameters other than size is excluded. The same experiments were carried out in dry and hydrated polyamide 6 to evaluate the effect of polymer matrix mobility in the "diffusion−migrant size" relationship. The experimental data were compared to well-known mathematical or semiempirical approaches, verifying that there is a relationship between the diffusion coefficient and the size of the migrant. However, it is demonstrated that this relationship is also affected by the mobility of the polymer matrix, becoming more pronounced as the mobility of the matrix decreases.

KEYWORDS: Diffusion coefficient; fluorescent recovery after photobleaching; dry and hydrated polyamide 6; polymer matrix mobility; molecular weight; molar volume

INTRODUCTION

Additives play a key role in all polymer technology fields, and plastic food packaging is not an exception. These compounds are frequently used to improve the processability and the properties of the polymeric matrix; however, as the final plastic product is brought into contact with food, there is always a risk of additive migration from the packaging plastic to the foodstuff. In addition, as plastic materials are not considered inert, there is always a risk of monomer or oligomer migration to the food. To ensure consumer health, European Union Directive 2002/72/European Commission for plastics (*1*) introduced limits to the overall migration and the specific migration of certain oligomers and additives. The migration of such substances has to be tested to show compliance with the food law (*1*). However, the experimental determination of the specific migration into food requires a considerable amount of time, if not being impossible in some cases due to technical or analytical problems. On the other hand, many scientific investigations have demonstrated in the past that migration from food-contact materials, as in plastic packaging, into food and food simulants is a predictable physical process (*2*, *3*), which follows Fick's laws of diffusion. Hence, in addition to the experimental methods, a new alternative tool appears to be applicable that is based on mathematical estimations. Many sophisticated mathematical models have been reported in the pertinent literature (*4*); however, estimation of the diffusion coefficient through such models can be so complicated and time-consuming as to render them impractical to use. Thus, the only practical way at present to predict diffusion through modeling relies on simpler empirical estimations that use a few easily accessible parameters. For simplicity in such approaches, the contribution of the diffusing molecule to the diffusion coefficient is evaluated only through its molecular weight, which is used as a general parameter to describe the molecule's size (*4*, *6*, *7*).

Piringer's model is one of the most used and well-known diffusion coefficient prediction models for plastic food-contact materials (*2*,*4*,*5*). This model (eq 1) is an empirical relationship of the predicted diffusion coefficient (D_P) with the molecular weight of the migrant (M_r), the temperature (T), and the polymer type, as expressed by A_p, a characteristic value of the polymer depending on its structure and temperature. The Arrhenius-type relationship between A_p and the parameters above is given as

$$D_P = 10^4 \exp\left[A_p - 0.1351 M_r^{2/3} + 0.003 M_r - \frac{10454}{T}\right] \quad (1)$$

$$A_p = A_p' - \frac{\tau}{T} \quad (2)$$

A_p, as expressed in eq 2, is a function of the athermal, dimensionless number A_p', a parameter associated with the "conductance" of the polymer matrix toward the diffusion of a substance, and τ,

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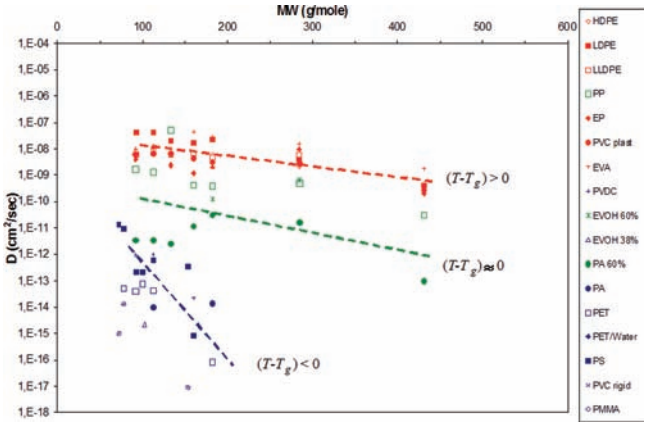
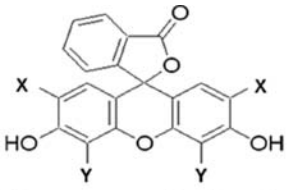


Figure 1. Diffusion behavior of different substances in polymers (data from Dole et al. (*6*)). Red points refer to diffusion data in polyolefins and rubbery polymers and blue points to diffusion data for glassy polymers. Green points show diffusion coefficients for polymers in intermediate states. Curves are only guides for the eyes.

a temperature parameter accounting for specific contribution of the polymer matrix to the diffusion activation energy. The parameter τ, together with the constant 10454 of eq 1, both with temperature dimensions, contributes to the activation energy, $E_a = (10545 + \tau) \times R$, where $R = 8.3145\,(\mathrm{J\,mol^{-1}\,K^{-1}})$ is the gas constant. Tables with values for both A_p' and τ are available for various polymers (*2*). For regulatory purposes, D_P is replaced by an overestimated D_P* to have a safety migration limit, which the packaging material should reassure is not exceeded. Equation 1 has been established by the compilation of numerous published diffusion coefficient data, predominantly of *n*-alkanes in polyolefins and by appropriate statistical treatment (*4*). The major advantage of this model is the fact that it requires only a few parameters to have a quick and safe estimation of *D*. It uses the molecular weight (MW) as a descriptor of the migrant's contribution to *D* and does not take into account the shape, volume, or chemical nature of the migrant. The resulting $D = f(\mathrm{MW})$ trend (where *f* is a function) is a straight line that linearly decreases as molecular weight increases. In addition, the same slope of reduction in the $D = f(\mathrm{MW})$ trend is predicted for all polymers, irrelevant of being in the rubbery or the glassy state.

Dole et al. (*6*) proposed a different approach regarding the effect of the migrant molecular weight on *D*. By correlation of numerous experimental diffusion data of various migrants with molecular weights up to 807 g/mol, it was shown that the $D = f(\mathrm{MW})$ trend is very different in polymers in the glassy state from that of polymers in the rubbery state (**Figure 1**). As shown in **Figure 1**, there is a continuous increase of the $D = f(\mathrm{MW})$ slope from rubbery polymers ($T - T_g > 0$; where T_g is the glass transition temperature) to glassy (high barrier) polymers ($T - T_g < 0$) when one is dealing with migrants heavier than 100 g/mol. Bearing in mind that E_a is the diffusion activation energy, which changes with increasing molecular weight, this new approach proves the basis that there is a variation of *D* and E_a dependence not only with the molecular weight of the migrant but also with the matrix mobility. Generally, matrix mobility is different from a polyolefin to a polyamide, but for a given matrix it can be greatly altered through temperature increase or plasticization. To summarize this approach, called hereafter in this paper the polymer matrix mobility or PMM approach, it may be stated that $D = f(\mathrm{MW})$ alone does not sufficiently describe the effect of migrant size in *D*, whereas $D = f(\mathrm{MW}, T - T_g)$ is a more appropriate expression, where the parameter $(T - T_g)$ accounts for the polymer matrix mobility.



Probe Name	X position	Y position
Fluorescein	H	H
2,7 Dichlorofluorescein	Cl	H
Eosin Y	Br	Br
Erythrosin B	I	I

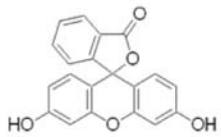
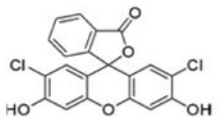
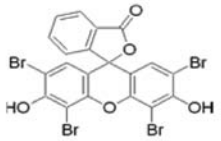
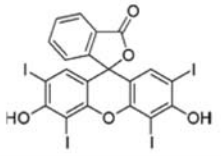
Figure 2. Core structure of the proposed model migrant series.

Besides the molecular weight parameter, other parameters related to the migrant known to affect *D* are the molecular volume, the shape of the molecule, or even the possible interactions between the molecule and the polymeric matrix (*8*, *9*). For this reason, a correlation of the diffusion coefficient with the molecular weight of commercial additives would be quite scattered, as is, for instance, the data in **Figure 1**, where the diffusivities of various migrants of different shapes and functionalities are correlated (*6*). It is obvious that to experimentally evaluate the aforementioned approaches, it is quite mandatory to use a series of homologous molecules with increasing molecular size. Equation 1 has been already tested by using a homologous series of alkanes (*4*, *9*, *10*), yet the shape of the *n*-alkanes is not typical of the commercial additives, providing unrealistic diffusivities for the tested molecular weight range. Pinte et al. (*11*) tried to overcome this problem by introducing a new series of molecules to evaluate such models, based on an "additive-shaped" probe on which methylene groups were added to increase molecular weight. The problem encountered in the latter approach was the fact that the shape of the molecules within the homologous series was not the same when large olefinic tails were added to produce higher molecular weight probes.

It is mandatory that a study regarding the effect of molecular weight on *D* should be based on a series of migrants ensuring that the shape and chemical functionality of the molecules within the series are the same regardless of the molecule size. In this work, we introduce an alternative probe series that can be used to investigate the critical relationship between *D* and the molecular weight for additives in food packaging polymers. The advantage and originality of the proposed migrant series are the fact that the shape and chemical functionality of the molecules within the series are ensured to remain the same regardless of the molecular weight. This is achieved by using molecules that are based on the same core molecule,- fluorescein (*12*). To increase the molecular weight, different halogen substituents are used in place of the hydrogen atoms of fluorescein, marked X and Y in **Figure 2**. The structures and properties of the probes used in the present study are summarized in **Table 1**. Moreover, fluorescein and its studied derivatives are all fluorescent probes that can be used to study diffusion through fluorescence microscopy.

The advantage of microscopic techniques and in particular fluorescence recovery after photobleaching (FRAP) (*11*, *13*−*15*), which was used in this study, is the fact that the diffusion coefficient of the fluorescent molecule within the matrix can be directly measured in a short period of time even for high-barrier matrices (*11*). Equally important, with FRAP we avoid any interactions of the matrix with other media. For instance, classic sorption tests or food simulant contact tests, which involve contact with a liquid, may lead to errors in the evaluation of *D* due to plasticization of the matrix or due to limitation of the mass transfer in the solid/liquid interface (*6*). In fact, microscopic techniques require only a small amount of the diffusing species to

Table 1. Structures and Properties of the Studied Molecules

Molecule	Structure	Molecular Weight (g/mol)	Molar Volume (cm^3/mol)
Fluorescein		332,1	188,7
2',7' Dichlorofluorescein		401,2	203,8
Eosin Y		647,89	231,4
Erythrosin B		835,89	248,5

be present in the matrix, excluding any possible plasticization of the matrix due to high quantities of the migrant (*16*, *17*).

MATERIALS AND METHODS

Materials. Polyamide 6 (PA6) was provided by DuPont de Nemours International S.A. (Geneva, Switzerland) in pellet form, having the commercial name Zytel 7301 NC010. Chemical structures of the fluorescent probes used as migrants in this study are presented in **Table 1**. All of the probes were supplied by Sigma-Aldrich. The molecular weights of the probes are as follows: fluorescein, 332.1 g/mol; 2′,7′-dichlorofluorescein, 401.2 g/mol; eosin Y, 647.9 g/mol; and erythrosin B, 835.9 g/mol.

Sample Preparation. All samples used in this study were prepared by thermopressing. Dried PA6 pellets were introduced in press mold and thermoformed at 240 °C into 50 μm thickness films. Meanwhile, saturated aqueous solutions of each probe were prepared at 40 °C. For the contamination step, the thermoformed polyamide films were immersed into the probe solutions for 0.5 h at 40 °C. After this step, the probed PA6 films were placed in a vacuum oven for 4 h at 80 °C to obtain dry probed samples, which were then quickly sealed between microscope slides with epoxy glue to ensure constant dry condition. Some PA6 films were also placed in different humidity environments directly after the drying step in order to have them stabilized in predetermined humid conditions. The selected environments were 54 and 75% relative humidities (RH), at 23 °C, produced by using saturated salt solutions (*18*). After at least 2 days of stabilization in the fixed environments, these samples were also sealed with epoxy glue between microscope slides to maintain constant water content throughout the diffusion experiments.

Methods. *Fluorescent Recovery after Photobleaching*. The diffusion coefficient of the four probes through PA6 was determined by FRAP experiments. FRAP was introduced for measuring diffusivities in biological systems (*13*); however, later studies demonstrated that it may also be used to determine slower diffusivities as the ones expected in polymer science (*11*, *14*, *15*). This technique is an ideal tool to study the mobility of molecules and particles on a microscopic level. A small region of a probed sample is photobleached by a brief exposure to an intense focused laser beam. The same, but attenuated, laser beam is then used to monitor the recovery of the fluorescence into the bleached region, as the fluorescent probes outside this region diffuse throughout it, eventually replacing the nonfluorescent probes in the initially bleached region. For the reported experiments, a DMIRE2 confocal microscope (Leica Microsystems, Wetzlar, Germany) was used with a 63× magnifying (number of aperture 1.4) oil objective. The film samples were inserted on the microscope stage, and the acquired picture was zoomed four times. By using the appropriate software, the line-bleaching pattern was selected having a rectangular shape in order to monitor diffusion in a single dimension (*19*). The pattern was deliberately selected as thin as possible to shorten the recovery time. A 20 mW helium−neon laser was used in full intensity to bleach the desired pattern. The fluorescence recovery was then monitored using the lowest possible intensity to avoid bleaching during reading of the fluorescent probes. Both bleaching and reading were performed at 488 nm for all samples. To improve the signal-to-noise ratio, the acquisition of the pictures was performed using a two-time line average mode. All experiments took place in an air-conditioned room, having a steady temperature of 23 °C. The acquired pictures were then filtered with a two by two median filter using the software ImageJ (U.S. National Institutes of Health, Bethesda, MD) before measuring the intensity recovery in the region of interest.

Differential Scanning Calorimetry (*DSC*). After the fluorescent recovery experiments in the confocal microscope, the specimens that had already been analyzed through FRAP were detached from the microscope glasses and the degree of crystallinity was determined by DSC analysis. All measurements were conducted in a TA MDSC2940 analytic device (TA Instruments, New Castle, DE), where the DSC was heated at a slow rate (10 °C min^{-1}) from 20 to 260 °C. For calculation, the heat of fusion for the 100% crystalline PA6 is considered to be 190 J g^{-1} (*20*).

Table 2. Crystallinity (X_c) and Melting Point Temperature (T_m) of the Polyamide 6 Samples Tested in Various Humidity Environments

	fluorescein	2,7-dichlorofluorescein	eosin Y	erythrosin B
dry				
X_c (%)	21.8 ± 0.4	18.7 ± 0.6	22.0 ± 0.3	21.8 ± 0.6
T_m (°C)	221.1 ± 0.3	220.4 ± 0.2	220.9 ± 0.6	220.5 ± 0.5
54% RH				
X_c (%)	24.8 ± 0.3	18.5 ± 0.4	21.3 ± 0.6	22.0 ± 0.7
T_m (°C)	220.56 ± 0.2	220.2 ± 0.3	218.6 ± 0.8	219.4 ± 0.2
75% RH				
X_c (%)	26,3 ± 0.8	22.7 ± 0.5	26.3 ± 0.3	23,5 ± 0.9
T_m (°C)	219.2 ± 0.4	220.5 ± 0.3	219.8 ± 0.4	220.0 ± 0.3

RESULTS AND DISCUSSION

Crystallinity Results. In semicrystalline polymers, such as PA6, the presence of crystals hinders the movement of the migrant in two different ways; (a) being impermeable, crystals increase the effective path of diffusion length (tortuous path) (*21*), and (b) they seem to reduce the polymer chains mobility in the amorphous phase, because chain ends are trapped in the neighboring crystalline lamellae, leading to a higher activation energy of diffusion (*22*). On the other hand, it is widely known that the absorption of water leads to substantial changes in the structure of polyamides even at ambient temperatures such as our experimental conditions (*23*). As water acts as a plasticizer by enhancing macromolecular mobility in the amorphous regions of polyamides, water-induced crystallization could be expected (*24*, *25*), which would alter the degree of crystallinity between the dry and hydrated samples. The experimental DSC crystallinity results are listed in **Table 2**. It is observed that a small increase of the crystallinity percentage occurs in the samples as relative humidity increases. Nevertheless, the differences are not so significant as to prevent a direct comparison of the acquired diffusion data between the dry and hydrated PA grades, as the maximum standard deviation of the degree of crystallinity for specimens probed with the same substance is 2.7% in the case of eosin Y probed PA6 samples, whereas the overall average standard deviation is 2.5%.

Diffusion Coefficient (D) and Activation Energy (E_a) Results. The first step in the analysis of the acquired fluorescent recovery images was to quantify the recovery of intensity and calculate the diffusion coefficient through appropriate mathematical treatment. By conducting FRAP experiments, one can monitor the recovery of the fluorescence into the bleached area, as the fluorescent probes

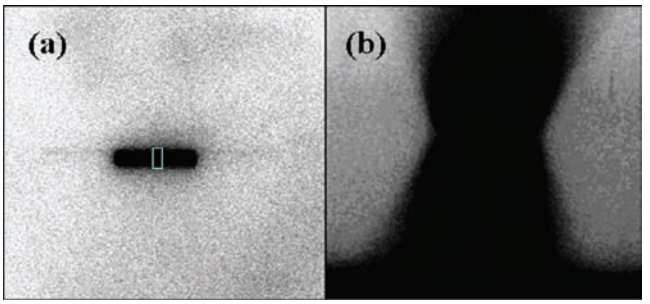


Figure 3. Example of the bleaching pattern in the initial stage of the FRAP experiment for the fluorescein-probed PA6 samples: (**a**) bleaching pattern in the *XY* direction (the white rectangular area in the middle indicates the ROI in which the fluorescence recovery was monitored); (**b**) bleaching depth in the *ZY* direction (the narrowest section of the bleached pattern in the *ZY* direction corresponds to **a**).

outside this area diffuse throughout the sample, eventually replacing the nonfluorescent probes in the initially bleached region. This process leads to the determination of the self-diffusion coefficient of the migrant (*26*, *27*). However, in low probe concentrations, when interactions between particles can be neglected, the self-diffusion coefficient becomes identical to the mutual diffusion coefficient, *D* (*28*, *29*).

The experimental planning ensured that diffusion took place only in one dimension; as shown in **Figure 3a**, the region of interest (ROI) in which fluorescence recovery was monitored was adequately narrow to ensure that diffusion occurred only from the unbleached regions above and beneath the ROI. In addition, bleaching occurred in all depths of the samples (**Figure 3b**), ensuring that there is no enrichment of the fluorescence due to fluorophore diffusion in the *Z* axis. The fluorescence recovery of the images over time was determined with the free software ImageJ, by selecting the ROI and comparing the image intensity in this specific region with the intensity of the background.

With regard to the assessment of *D*, the following equation was used, derived from Fick's second law, as described elsewhere (*11*), with the assumption that the mild contamination conditions that were followed lead to adequately low probe concentration in the specimens so as to neglect any crowding effects:

$$\%\ \text{recovery} = \frac{I_t}{I_\infty} = \frac{M_t}{M_\infty} = \int_{-1}^{1} \frac{C_t}{C_\infty}(z,\text{Fo}) = \int_{-1}^{1} \frac{1}{2}\left(\text{erf}\left\{\frac{1-z}{\text{Fo}}\right\} + \text{erf}\left\{\frac{1+z}{\text{Fo}}\right\}\right) \quad (3)$$

I_∞, M_∞, and C_∞ are, respectively, the fluorescence intensity, probe amount, and probe concentration in equilibrium, and I_t, M_t, and C_t are the relevant parameters at time t. The parameter z is equal to x/h, where x is the location of the probe at time t and h is the half width of the ROI. Fo is the parameter that connects the intensity recovery with *D*, the diffusion coefficient, as

$$\text{Fo} = \sqrt{Dt}/h$$

.

Values of *D* of the four probes for the dry and hydrated states at 23 °C, obtained through eq 3, are listed in **Table 3**. From these values, it is observed that the diffusion coefficient is substantially decreased as the size of the migrant increases, in all mobility states of the matrix. This observation is attributed to the larger free volume size requirement for the diffusion step of the increasingly larger migrants. Numerous studies have shown that an inverse variation of the diffusion coefficient with parameters describing

Table 3. Diffusion Coefficients (cm^2/s) of the Studied Molecules at 23 °C in Polyamide 6

	dry samples	54% RH	75% RH
fluorescein	25×10^{-15}	97×10^{-15}	320×10^{-15}
2,7-dichlorofluorescein	8.2×10^{-15}	60×10^{-15}	270×10^{-15}
eosinY	0.35×10^{-15}	25×10^{-15}	95×10^{-15}
erythrosin B	0.08×10^{-15}	10×10^{-15}	77×10^{-15}

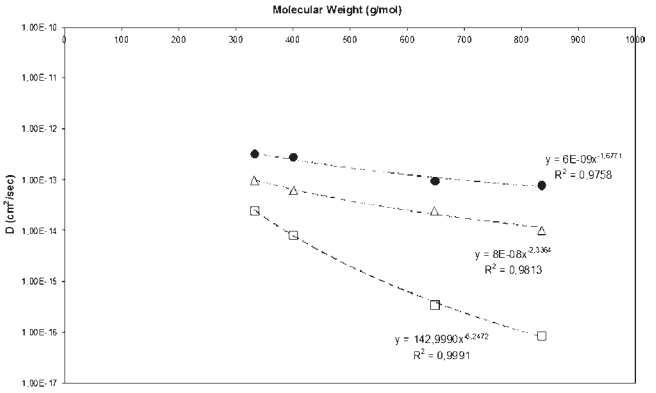


Figure 4. Diffusion coefficients of the PA6 samples at 23 °C as a function of molecular weight: (□) dry samples; (△) 54% RH stabilized samples; (●) 75% RH stabilized samples. The dotted lines are fits of eq 4 in the experimental results.

the size of the molecule exists, such as the molecular weight, the number of carbon atoms, or the molar volume (*8*−*10*, *30*, *31*). It has also been reported (*32*, *33*) that this inverse relationship between the migrant size and *D* can be quantified through a power law as shown in eq 4, by using molecular weight as a descriptor of the molecule size.

$$D = bM^a \quad (4)$$

D (cm^2/s) is the diffusion coefficient, *M* (g/mol) is the molecular weight of the migrant, and *a* and *b* are characteristic parameters of the matrix.

Our experimental data for the dry and hydrated states have been successfully fitted ($R^2 > 0.98$) to eq 4 as shown in **Figure 4**, showing that the power law is valid for the diffusion of the proposed probe series through the polyamide matrix. The parameters *a* and *b* were evaluated through eq 4. Values of *a* were between −6.25 for the dry state and −1.68 for the PA6 samples stabilized in 75% RH. This increasing relationship of *a* with the water content is attributed to the free volume and chain mobility increase due to water-induced plasticization. In fact, **Table 3** shows also that the decrease of the diffusion coefficient versus molecular weight is more pronounced in the dry PA6 samples than in the plasticized ones.

It is worthwhile to note that eq 4 takes into account only the molecular weight of the migrant as the only parameter affecting *D*, ignoring any other factors, such as the shape of the migrants (*30*, *34*) or even specific interactions between the matrix and the migrant, which have been reported to substantially affect *D* (*8*, *9*). In other words, the almost perfect fit of the experimental *D* results in eq 4 is due to the use of this homologous series of probes, having the same interactions with the matrix and similar spherical shape, regardless of their increasing size.

The experimental *D* results of **Table 3** indicate an increase of the diffusion coefficient with humidity for a given probe. This observation can be explained by taking into account the humidity plasticization effect on polyamides; water molecules act as a

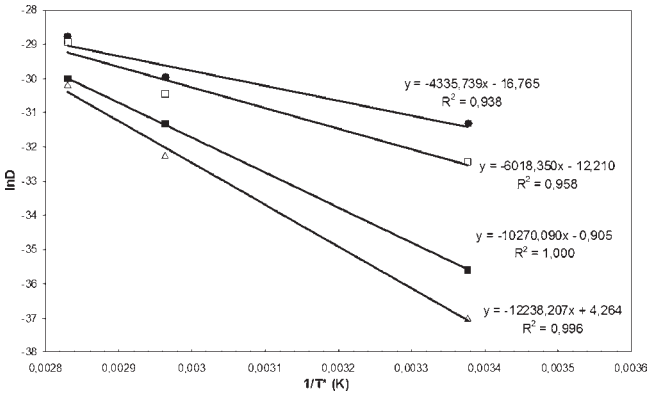


Figure 5. Arrhenius type plots for the experimental results: (●) fluorescein; (□) 2′,7′-dichlorofluorescein; (■) eosin Y; (△) erythrosin B. T^* is an artificial temperature associated with humidity-induced plasticization as expressed in eq 6.

plasticizer in the hydrophilic PA matrix, increasing the free volume of the amorphous phase. The larger free volume leads to a substantial decrease of the glass transition temperature (T_g) of PA, resulting in increases of matrix mobility (*23*, *35*), but also it is easier to achieve diffusion steps for a given probe, due to the greater free volume of the matrix. The aforementioned humidity-induced plasticization dependence of the diffusion coefficients was further analyzed on the basis of the exponential-type equation

$$D = D_o \times e^{(-E_a/RT^*)} \quad (5)$$

where E_a is the activation energy of diffusion (kj/mol), D_o is the Arrhenius front factor, and R is the gas constant. T^* is an artificial temperature, associated with plasticization; the presented experiments were conducted in a steady temperature (23 °C); however, the $T - T_g$ temperature of the specimens was different for the various relative humidity levels. Considering the parameter ($T - T_g$) as a descriptor of the plasticization contribution to the diffusion activation, it is feasible to calculate an "artificial temperature", T^*, by the relationship

$$T^* = T_{exptl} + (T_{gd} - T_{gh}) \quad (6)$$

In eq 6, T_{exptl} is the experimental temperature (23 °C), T_{gd} is the glass transition temperature of the PA6 in dry conditions, and T_{gh} is the glass transition temperature in hydrated PA6 samples treated in different relative humidity environments. The T_g values in each humidity environment were taken from previously published data (*35*). On the basis of the relevant plots of eq 5 (**Figure 5**), the apparent activation energy values as expressed from the artificial temperature T^* were found in the range of 36.1−101.8 kJ/mol (**Table 4**), which are quite low for polyamides, especially for bulky migrants such as the ones studied (*6*). However, it should be taken into account that calculations are based on plasticized samples. The activation energy, E_a, is considered as the necessary energy for the separation of the macromolecular chains by cooperative motions of sufficient amplitude to allow the migrant to execute its diffusional jump (*22*). As a result, E_a is a function of the inter- and intrachain forces that must be surpassed to allow the diffusing molecule to transport. Plasticizers, as is water for PAs, separate the macromolecular chains, leading to an increase of the free volume and also a decrease of the intermolecular forces, resulting in lower energy requirements for the separation of the chains. On the other hand, as expected, activation energy is found to increase with increasing migrant size, suggesting that more complex segmental motions are needed to provide the necessary free volume for the larger molecules to diffuse (*6*).

Table 4. Activation Energy for the Studied Probes in PA6, Calculated through Equation 5

probe	activation energy (kJ/mol)
fluorescein	36.05
2,7-dichlorofluorescein	50.04
eosin Y	85.39
erythrosin B	101.75

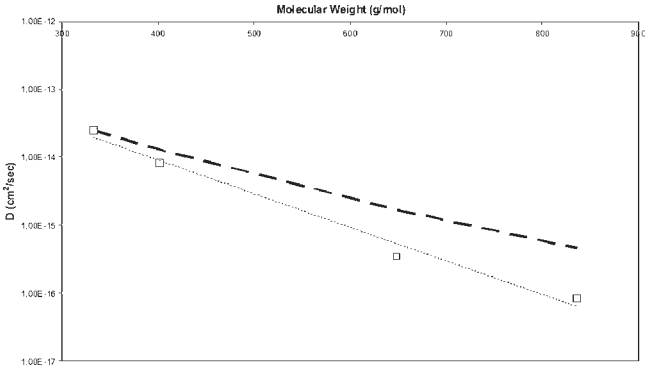


Figure 6. Experimental data comparison with predicted values from eq 1 at 23 °C: (□) dry PA6 data; (- - -) predicted data from eq 1. Predicted values are normalized to the experimental D value of fluorescein for comparative reasons.

Influence of Migrant Size on the Probe Diffusion Coefficient. Diffusion coefficients as a function of molecular weight are presented in **Figure 4**. As discussed earlier, the data may be fitted in a power law (eq 4), which almost resembles a straight line. However, it is observed that the "slope" of the $D = f(MW)$ relationship is very different in the dry samples in comparison with the hydrated samples. In fact, the higher the water quantity in the samples, the less D is affected by the molecular weight increase of the probe. The same statement can be made by realizing the term "higher water quantity" within the PA samples as "increased plasticization" of the samples, or even as higher ($T - T_g$) values of the matrix.

Bearing this in mind, it would be worthwhile to compare the diffusion results with the predictions of Piringer's equation (**Figure 6**) and also with the PMM approach (**Figure 7**). Comparison with the Piringer equation was feasible only for the dry state as plasticization cannot be taken into account by eq 1. As the A_p' and τ parameters of eq 2 are not known for PA6, the relevant published parameters of PA66 were used for the calculations, that is, $A_p' = 2.0$ and $\tau = 0$ (*2*). On the other hand, the PMM approach, which is an attempt to be more universal with regard to matrix mobility, has correlated many data, among them data of plasticized polymers such as PVC or PET plasticized by ethanol (*6*). As a result, a direct comparison of all the experimental data with the PMM approach was feasible. The first conclusion derived from observing **Figure 6** is that the experimental data of the dry matrix seem to be close to eq 1 predictions for the D−molecular weight relationship. There is of course a larger slope in the experimental $D = f(MW)$ trend, but the difference is not so pronounced. On the other hand, it must be noted that the change observed in the $D = f(MW)$ slope for higher plasticization, in comparison with the slope of dryer samples, confirms the PMM approach (**Figure 7**). The higher the water plasticization, the less D was affected by the size of the probes, verifying the suggestion that the $D = f(MW)$ trend becomes almost a parallel

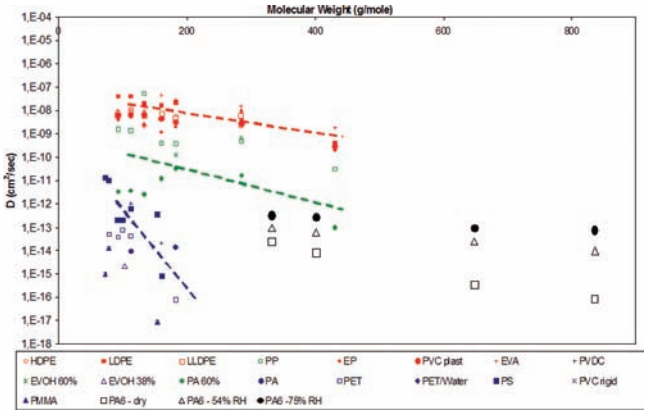


Figure 7. Comparison of the experimental *D* results with data from Dole et al. (*6*): (□) dry samples; (△) 54% RH stabilized samples; (●) 75% RH stabilized samples. Curves are only guides for the eyes. Red points refer to diffusion data in polyolefins and rubbery polymers and blue points to diffusion data for glassy polymers. Green points show diffusion coefficients for polymers in intermediate states.

line when $(T - T_g)$ values of the matrix are high (rubbery state), but there is a greater effect of MW on *D* at lower $(T - T_g)$ values of the polymeric matrix. In the studied case, the slope of the $D = f(\mathrm{MW})$ trend for the samples stabilized at 75% RH was found to decrease 68.8% when compared with the relevant slope of the 54% RH stabilized samples and as much as 91.8% when compared with the relevant slope of the dry PA6 samples.

However, comparison of previously published diffusion data with the experimental results (**Figure 7**) shows that the dependence of *D* on the MW of organic substances without heavy halogen substituents (as the ones tested in ref *6*) is significaly different from the presented experimental correlations. This is attributed to the fact that the wide mass range within the set of the tested migrants is primarily determined from the very different masses of the halogen substituents (**Figure 2**). As a result, further investigation of this comparison between the experimental data and the known models has to take into account the shape and volume of the diffusing molecules. Previous studies have drawn useful conclusions by correlating *D* with the molar volume of the migrant (*8*, *9*). The probe series that was tested in our experiments has many advantages such as the constant spherical shape and the fact that the interactions with the matrix are of the same nature regardless of the molecular weight; but as shown in **Table 1**, the molar volume of the probes does not significantly change as the molecular weight does. Comparison of the molecular weight of fluorescein with that of its heaviest derivative within the studied series, erythrosin B, reveals a 151.7% difference in the molecular weight of the two probes, whereas the molar volumes of the two migrants vary by only 31.7%. This fact could lead to misjudgments regarding the effect of the migrant size on *D*, if only molecular weight is considered as a descriptor of the migrant size. **Figure 8** presents a correlation of the experimental diffusion coefficient results with the molar volume (MV), calculated by using the software Spartan'08 (Wavefunction, Inc.) (*36*). By comparison of this correlation with the relevant figure for the molecular weight (**Figures 2** and **7**), it is obvious that the $D = f(\mathrm{MV})$ correlation is more severe than the experimental $D = f(\mathrm{MW})$ correlation and, surprisingly, **Figure 8** is in fact similar to the proposed PMM trend for the $D = f(\mathrm{MW})$ relationship for polymers under the glass transition temperature, such as PA6. In other words, the molar volume seems to be a more critical parameter to describe the variation of diffusion due to migrant size.

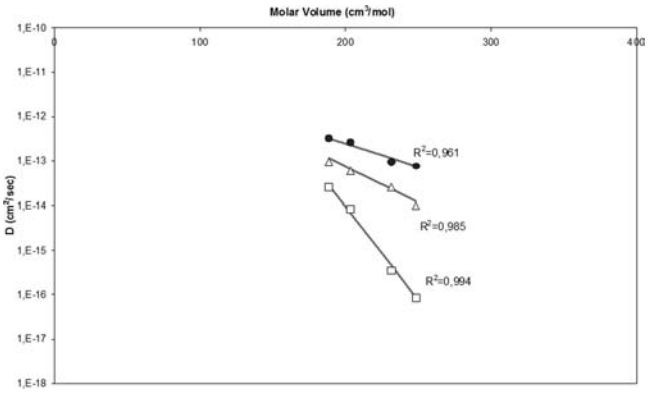


Figure 8. Diffusion coefficients of the PA6 samples at 23 °C as a function of molar volume: (□) dry samples; (△) 54% RH stabilized samples; (●) 75% RH stabilized samples. The lines represent the predictions of eq 7.

With this in mind, a quantification of the molar volume effect on *D* could be also considered by taking into account the effect of matrix mobility on the $D = f(\mathrm{MV})$ correlation, as the PMM approach suggests. The relevant analysis leads to the following empirical equation:

$$\ln D = b - (0.282 - 0.059 \ln T^*)\mathrm{MV} \qquad (7)$$

T^* accounts for the matrix mobility according to eq 6, and *b* is a constant equal to −12.62 for the dry PA6 samples, −22.93 for the 54% RH stabilized samples, and −23.74 for the 75% RH stabilized samples. As shown in **Figure 8**, eq 7 adequately describes the experimental diffusion data within the experimental conditions, incorporating the concept that the diffusion of a migrant in a polymer is affected not only by the size of the migrant but also by the matrix mobility.

In summary, the scope of the presented work is the investigation of the migrant size effect in the diffusion process and the subsequent evaluation of the critical relationship between *D* and the molecular weight for additives in food packaging polymers. For this matter, an original model migrant series is introduced, covering a wide molecular weight range from 332 to 836 g/mol. The advantage of the studied migrant series is the fact that it consists of probe molecules based on the same fluorescent core structure and having different sizes due to bulkier halogen substituents. *D* values of the fluorescent probes considered were assessed in dry and hydrated PA6 samples through FRAP. It was verified that the PMM model is a more realistic approach for the effect of the migrant size on *D*; however, considerations have to be made regarding the parameter describing the size of the diffusing molecule. An empirical relationship regarding the diffusion of the studied migrant series in dry and hydrated PA6 samples is also presented, based on the PMM approach.

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