JOURNAL OF Applied Polymer SCIENCE

Determination of the Activation Energies of Diffusion of Organic Molecules in Poly(ethylene terephthalate)

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ABSTRACT: Poly(ethylene terephthalate) (PET) is a highly inert packaging material that exhibits low interaction with foodstuff and consequently a limited diffusion of migrants. Migration modeling can therefore be used as an alternative to experimental migration tests in order to confirm compliance of PET packaging materials with food laws. The most important factor for predicting migration using mathematical models is the diffusion coefficient of the migrant in PET. However, current models that predict this parameter are typically based on worst-case scenarios and thereby significantly over-estimate the degree of migration. The key parameter for developing more realistic migration models is the activation energy of diffusion of potential migrants in PET, but experimental data on this are scarcely available in the scientific literature. The aim of the present study was therefore to develop a fast and precise method for determining diffusion coefficients and activation energies of diffusion of organic compounds in PET. Activation energies of diffusion for 13 organic compounds in PET were determined via their diffusion coefficient temperature dependencies. The molecular weight and activation energy of diffusion for the compounds investigated in this study were correlated, offering a basis for a new approach in predicting diffusion coefficients for use in migration modeling. The proposed method is a suitable tool to establish the datasets needed to refine the current migration model. © 2012 Wiley Periodicals, Inc. J. Appl. Polym. Sci. 128: 3885–3892, 2013

KEYWORDS: packaging; polyesters; theory and modeling; kinetics

Received 22 May 2012; accepted 21 September 2012; published online 12 October 2012
DOI: 10.1002/app.38623

INTRODUCTION

Poly(ethylene terephthalate) (PET) is one of the most inert materials used for packaging applications. PET bottles and trays exhibit very low interactions with foodstuff. In addition, PET contains only small amounts of additives and residual monomers like ethylene glycol or terephthalic acid. The high inertness of PET combined with the low concentrations of potential migrants lead to limited migration of monomers, catalysts, or impurities from the polymer into the food. Consequently, experimental studies attempting to determine the migration of monomers and additives through PET have mostly failed due to insufficient detection limits of the analytical test methods employed. Migration modeling therefore offers a useful alternative to experimental migration tests that can be used to confirm compliance of PET packaging materials with food laws.

The most important factor for predicting migration using mathematical models is the diffusion coefficient of a migrant in PET. If the diffusion coefficient at a certain temperature is known, the migration can be calculated according to eq. (1).[1] In this equation, $m_{F,t}/A$ is the area-dependent mass transfer of a migrant into the food/simulant. The initial concentration of the migrant in the polymer (before the migration experiment) is $c_{P,0}$. D_P is the diffusion coefficient and t is the storage time. q_n is a mathematical correction factor. The parameters ρ_P and d_P are the density of the polymer and the wall thickness of the packaging material, respectively. The parameter α is defined in eq. (2) as the ratio of the volume of the foodstuff V_F to the volume of the packaging V_P and the partition coefficient $K_{P,F}$.

$$\frac{m_{F,t}}{A} = c_{P,0}\ \rho_P\ d_P\left(\frac{\alpha}{1+\alpha}\right)\left[1-\sum_{n=1}^{\infty}\frac{2\alpha(1+\alpha)}{1+\alpha+\alpha^2 q_n^2}\,e^{\left(-D_P\,t\frac{q_n^2}{d_P^2}\right)}\right] \quad (1)$$

$$\alpha = \frac{1}{K_{P,F}}\frac{V_F}{V_P} \quad (2)$$

Determining the diffusion coefficient D_P from experimental migration kinetics into food simulants is a very time-consuming and laborious process. Consequently, data for diffusion coefficients are scarcely available in the scientific literature and empirical equations have therefore been developed to predict the diffusion coefficients of potential migrants. Typically, diffusion coefficients are predicted from the molecular weight of the

migrants. An example of such an approach is given in eq. (3),[2,3] which is currently the recommended method for predicting diffusion coefficients in packaging polymers.[4] In this equation the parameter A_P^* has been introduced as a simplified numerical representation describing the diffusion behavior of a given polymer. In general, a larger A_P^* value leads to a higher diffusion coefficient D_P of the migrant in the polymer. A_P^* is also a function of the temperature, as given in eq. (4). In this equation, the polymer-specific term τ represents a portion of the activation energy of diffusion of a migrant in the polymer. The relationship between τ and the activation energy of diffusion E_A is given in eq. (5), where R is the gas constant (8.3145 J mol^{-1} K^{-1}). According to eq. (3), A_P^* can be used to comfortably predict the diffusion coefficient D_P of a potentially migrating organic molecule in PET as a function of the molecular weight of the migrant and the temperature. In this model, $A_P'^*$ and τ are defined in such a way that the resulting diffusion coefficients are based on a worst-case value for the molecular weight of the migrant, which means that the predicted diffusion coefficients are in any case higher than under real migration conditions.[4] The currently recognized $A_P'^*$ values for PET are $A_P'^* = 6.4$ at temperatures above the glass transition temperature T_g and $A_P'^* = 3.1$ below T_g.[4] Both values are used in combination with $\tau = 1577$ K. According to eq. (5), $\tau = 1577$ K corresponds with activation energy of 100 kJ mol^{-1} for any migrant.

$$D_P = 10^4 e^{A_P^* - 0.1351M^{2/3} + 0.003M - \frac{10454}{T}} \quad (3)$$

$$A_P^* = A_P'^* - \frac{\tau}{T} \quad (4)$$

$$E_A = (10454 + \tau)R \quad (5)$$

In our previous studies[5–7] we reported that the above parameters for PET lead to a significant over-estimation of migration. This is mainly because the activation energy of diffusion in PET in the current model is set to 100 kJ mol^{-1}, regardless of the migrant in question.[7] However, high molecular weight compounds are expected to have an activation energy of diffusion that is significantly higher than this value. As a result, prediction of diffusion coefficients of migrants in PET based on this value, in combination with an estimation of the temperature dependency of migration, is incorrect. Another important factor outlined in our previous studies[5] concerns the 95% ethanolic solutions that are commonly used as food simulants for experimentally determining diffusion coefficients in PET for latter use in migration models. Ethanol significantly swells the PET polymer. As a result, use of 95% ethanol as a food simulant leads to a substantial increase in migration. From a food law compliance perspective, such over-estimation is uncritical because the predicted migration will be higher than the experimentally-determined values. As long as these predicted migration values remain below the legally-specified migration limits for the migrants of interest, compliance of the PET bottle with food laws is given. The safety margin or degree of over-estimation in this case, however, is not exactly known. In conclusion, although migration modeling is a powerful tool for predicting migration, current migration models are based on variable parameters that have been estimated using experimental data. Such parameters are valid only for the experimental conditions with which they were estimated. If the diffusion coefficients used for the parameterization of the model were determined under swelling conditions, the migration models will consequently also be over-estimative. For more realistic migration calculations, e.g., for consumer exposure evaluation, over-estimation of the migration is not desirable. Therefore, more accurate modeling parameters should be made available. An important result and the main conclusion of our previous study is that the key parameter to establish more realistic migration models is the activation energy of diffusion of potential migrants in the PET polymer.[7] These activation energies of diffusions can be applied either directly through the activation energy approach of the migration models or through recalculation into more realistic and variable τ values for modeling migration from PET.

The aim of the present study was therefore to develop a fast and precise method for determining diffusion coefficients and activation energies of diffusion of organic compounds in PET up to temperatures of about 200°C. Such high temperatures are necessary for determining activation energies of diffusion of higher molecular weight compounds in PET. In addition, a high temperature leads to a fast migration into the gas phase and excludes swelling of the polymer from any solvent. Finally, the activation energy of diffusion was determined from the temperature dependency of the diffusion coefficients using the Arrhenius approach.

MATERIALS AND METHODS

Selection of the Surrogates

Model compounds were used as surrogates for real contaminants in PET because PET bottles with real contaminants in the molecular weight range of interest are rarely available. The following model contaminants (surrogates) were chosen for the migration kinetics assessments: toluene (CAS No. 108-88-3), chlorobenzene (CAS No. 108-90-7), phenyl cyclohexane (CAS No. 827-52-1), benzophenone (CAS No. 119-61-9), and methyl stearate (CAS No. 112-61-8). These compounds are widely used in the evaluation of cleaning efficiencies of PET recycling processes or as model compounds for migration kinetics. They represent the four general categories: volatile and nonpolar, volatile and polar, nonvolatile and nonpolar, and nonvolatile and polar. In addition, the following *n*-alkanes were used: octane (CAS No. 111-65-9), decane (CAS No. 124-18-5), dodecane (CAS No. 112-40-3), tetradecane (CAS No. 629-59-4), hexadecane (CAS No. 544-76-3), octadecane (CAS No. 593-45-3), eicosane (CAS No. 112-95-8), docosane (CAS No. 629-97-0), and tetracosane (CAS No. 646-31-1). The solvent tetrahydrofurane (CAS No. 109-99-9) was the only real PET contaminant used in these tests.

Preparation of the Spiked PET Bottles

The PET bottles used for the migration kinetics were prepared according to the following procedures:

Bottle A: 50 g of octane, decane, dodecane, tetradecane, hexadecane, octadecane, eicosane, docosane, and tetracosane were mixed to give a solution of 450 g. This mixture was added at a nominal concentration of 200 ppm per substance to the PET melt during preform manufacturing using the liquid colorant port of the

Table I. Experimentally Determined Diffusion Coefficients from Bottles A to C

Model compound [molecular weight (g mol^{-1})]	Concentration in PET (mg kg^{-1})	Temperature (°C)	Diffusion coefficient (cm^2 s^{-1})
Tetrahydrofuran (72)	8.7	121	1.31×10^{-10}
		141	9.75×10^{-10}
		159	5.16×10^{-9}
		180	1.21×10^{-8}
Toluene (92)	203	121	8.04×10^{-10}
		141	6.20×10^{-9}
		161	3.82×10^{-8}
		180	9.06×10^{-8}
Chlorobenzene (113)	253	121	1.96×10^{-9}
		141	1.42×10^{-8}
		161	8.46×10^{-8}
		180	1.96×10^{-7}
Decane (142)	22	120	3.63×10^{-12}
		141	1.14×10^{-10}
		161	2.63×10^{-9}
		179	2.96×10^{-8}
Phenyl cyclohexane (162)	641	121	2.24×10^{-11}
		141	4.38×10^{-10}
		161	4.14×10^{-9}
		180	1.67×10^{-8}
Dodecane (170)	85	120	1.97×10^{-11}
		141	3.68×10^{-10}
		161	3.43×10^{-9}
		179	1.18×10^{-8}
Benzophenone (182)	786	121	1.19×10^{-10}
		141	1.94×10^{-9}
		161	1.52×10^{-8}
		180	5.51×10^{-8}
Tetradecane (198)	162	120	8.16×10^{-12}
		141	1.80×10^{-10}
		161	1.95×10^{-9}
		179	7.47×10^{-9}
Hexadecane (226)	125	120	1.78×10^{-11}
		141	4.89×10^{-10}
		161	5.31×10^{-9}
		179	2.15×10^{-8}
Octadecane (254)	71	120	5.26×10^{-11}
		141	1.52×10^{-9}
		161	1.76×10^{-8}
		179	7.74×10^{-8}
Eicosane (282)	129	120	1.09×10^{-11}
		141	3.56×10^{-10}
		161	4.27×10^{-9}
		179	2.07×10^{-8}
Methyl stearate (298)	792	121	1.67×10^{-11}
		141	4.82×10^{-10}
		161	5.70×10^{-9}
		180	2.39×10^{-8}
Docosane (310)	200	120	3.10×10^{-12}
		141	1.02×10^{-10}
		161	1.39×10^{-9}
		179	6.82×10^{-9}

preform machine. The preforms were then blown to bottles of 500 mL volume.

Bottle B: Neat surrogates of toluene (0.5 g per kg PET), chlorobenzene (0.5 g per kg PET), phenyl cyclohexane (0.8 g per kg PET), benzophenone (1.0 g per kg PET) and methyl stearate (1.0 g per kg PET) were given to dried virgin PET pellets. The contaminated batches were kept under a nitrogen atmosphere at 38°C for 7 days with periodical agitation. The contaminated material was then used without further predrying for manufacturing PET preforms. The preforms were shipped to a bottle manufacturing plant where they were blown to 300 mL PET bottles.

Bottle C: A single bottle (500 mL) was purchased from a PET bottle manufacturer. The PET of the bottle contained tetrahydrofurane, which was most probably from contamination of the colorant master batch.

Determination of the Bottle Wall Concentrations

After the bottle manufacturing process, the bottle wall concentrations of the model compounds in the spiked test bottles were determined according to the procedures given below. The concentrations of the migrants in the test bottles are summarized in Table I.

The model compounds in bottle A were determined according to the following procedure: For each test, 1.0 g of the PET material was extracted with 10 mL dichloromethane and stored at 40°C for 3 days. The extracts were then analyzed by gas chromatography with flame ionization detection (GC-FID): Column: DB 1-20 m-0.18 mm i.d.-0.18 µm film thickness, temperature program: 50°C (2 min), followed by heating at 10°C min^{-1} to 340°C (15 min), prepressure: 50 kPa hydrogen, split: 10 mL min^{-1}. Calibration was achieved by standard addition of the model compounds. *tert*-Butylhydroxyanisole (BHA, CAS No. 8003-24-5) and Tinuvin 234 (CAS No. 70321-86-7) were used as internal standards.

The model compounds in bottle B were determined according to the following procedure: 1.0 g of each PET sample was placed in a 5 mL glass vial. One milliliter 1,1,1,3,3,3-hexafluoro-*iso*-propanol (HFIP) was given to the PET material and stored for 1 day at 60°C in order to swell the PET matrix. Then, 2.0 mL *iso*-propanol was added and stored for a further 1 day at 60°C to extract the swollen matrix. The extract was decanted from the polymer and stored at 4°C for 8 h. The extracts were then decanted again from the precipitate and analyzed by GC-FID: Column: SE10-30 m-0.32 mm i.d.-0.32 µm film thickness, temperature program: 40°C (5 min), rate 15°C min^{-1}, 240°C (15 min), pressure: 50 kPa hydrogen, split: 10 mL min^{-1}. Quantification was achieved by external calibration using the standard addition method. Parts of a standard solution of the surrogates in *iso*-propanol were added to uncontaminated PET flakes and were analyzed together with the PET samples from the contamination experiments.

Tetrahydrofurane in bottle C was determined by headspace GC-FID. Quantification was achieved using stock solutions of tetrahydrofurane in toluene. Column: ZB 1-30 m-0.25 mm i.d.-0.32 µm film thickness, temperature program: 50°C (4 min), followed by heating at 20°C min^{-1} to 320°C (15 min), prepressure: 50 kPa helium, split: 10 mL min^{-1}. Headspace autosampler: Perkin Elmer HS 40 XL, oven temperature: 200°C, needle temperature: 210°C, transfer line: 210°C, equilibration time: 1 h, pressurization time: 3 min, injection time: 0.04 min, withdrawal time: 1 min.

Migration Kinetics

Migrations into the gas phase of the spiked model compounds were determined using an automated method that involved placing strips of 1.0 × 3.5 cm^2 in a cylindrical migration cell (diameter: 14 mm, length: 150 mm). The wall thickness of all bottle wall strips was around 0.3 mm. The surface area of the tests strips including the cut edges was calculated to be 7.3 cm^2. The migration cell was heated and the compounds migrating from the PET bottle wall strips were purged out of the extraction cell by a helium stream of 20 mL min^{-1}. The migrants were trapped (Carbopack B 20 mm, Supelco) at a trap temperature of −50°C (Peltier element). The loaded trap was completely desorbed and transferred directly to the GC every 30 min by heating it to 350°C within 10 s. Subsequently, a new trapping cycle started. The migrants were separated and quantified during the chromatographic measurements. Calibration was achieved by injection of neat standard solutions of the migrants into the migration cell. Gas chromatograph: Column: DB1, length: 30 m, inner diameter: 0.32 mm, film thickness 1.0 µm. Temperature program: 120°C (2 min), rate 20°C min^{-1}, 320°C (21 min), pressure 70 kPa helium, detector temperature: 320°C.

Determination of the Diffusion Coefficients and Activation Energies

The diffusion coefficients of the model compounds in PET were determined from their migration kinetics into the gas phase. The area-dependent migration (in cm^2 s^{-1}) correlated with the reciprocal square root of time (in $s^{1/2}$). The diffusion coefficients were calculated according to eq. (6).[1] This equation is applicable for the experimental determination of diffusion coefficients for migration up to about 60% of the mass transfer of the migrant.[2] The activation energies of diffusion were then calculated from the temperature dependency of the diffusion coefficients using the Arrhenius approach [eq. (7)]. In eq. (7), R is the gas constant and E_A is the activation energy of diffusion (in J mol^{-1}). D_0 is a pre-exponential factor (in cm^2 s^{-1}), and T is the temperature (in K). According to eq. (7), the natural logarithm of D_P is inversely proportional to temperature. Activation energies of diffusion were calculated from the slope of this correlation ($-E_A/R$). To accurately determine the Arrhenius plot it is important to establish a suitable temperature range. The diffusion at the highest temperature is very fast so that only about 3–4 points are available for the linear correlation. Conversely, diffusion at the lowest temperature is very slow. A temperature range between 120°C and up to 180°C was determined in pretests to be the most suitable for PET.

$$\frac{m_{F,t}}{A} = \frac{2}{\sqrt{\pi}} c_{P,0} \sqrt{D_P\, t} \tag{6}$$

$$D_P = D_0\, e^{-\frac{E_A}{RT}} \tag{7}$$

RESULTS AND DISCUSSION

The determination of diffusion coefficients is typically very difficult for PET because this process for organic molecules in PET is very slow at low temperatures. Consequently, experimentally-determined concentrations of migrants in the food simulants under typical testing conditions (e.g., at 40°C for 10 days) are generally very low and the diffusion coefficients derived from such tests often have large errors. The mass transfer from the packaging material to food (simulants) at higher temperature increases significantly. However, only a few food simulants, e.g. miglyol or olive oil, are suitable for migration tests at temperatures above 100°C. Additionally, swelling of the polymer matrix can occur in some cases, which increases the diffusion coefficients.

Within the present study, an automated method for determining the migration of organic compounds from PET bottle wall strips into the gas phase at high temperatures was developed. The basic principle of this method was published by Vandenburg and Gramshaw,[8] who used a cylindrical migration cell with a constant nitrogen flow and trapped the migrated substances on Tenax®. The Tenax® was then exchanged and subsequently extracted with diethylether, as is standard practice. After spiking with an internal standard, the diethylether solution was analyzed by GC. Our study used principally the same approach. However, the focus of our method development, was to automate and speed up the sample treatment by coupling the migration cell and pretrap directly to a GC using thermal desorption rather than solvent extraction. This faster method allows diffusion coefficients to be determined at high temperatures, whereby the total mass transfer of the migrant into the contact medium is completed within only a few hours. With our improved method it was possible to measure the migration into the gas phase at intervals of about 30 min. This rapid method for determining migration generates a large number of kinetic data points per sample, thereby allowing a precise determination of the migration kinetics and consequently a more realistic determination of the diffusion coefficients in PET. It should be noted here, however, that this study concerns only diffusion inside solid PET and not from the PET surface into any food or food simulant.

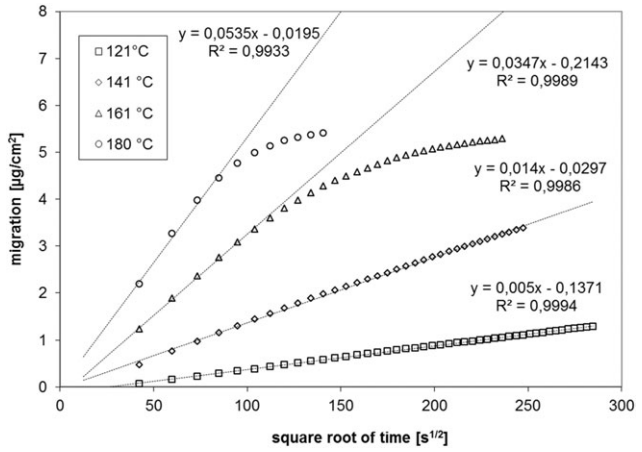

Figure 1. Migration of toluene from PET into the gas phase at temperatures between 121 and 180°C ($A = 7.3$ cm^2, $c_{P,0} = 203$ ppm).

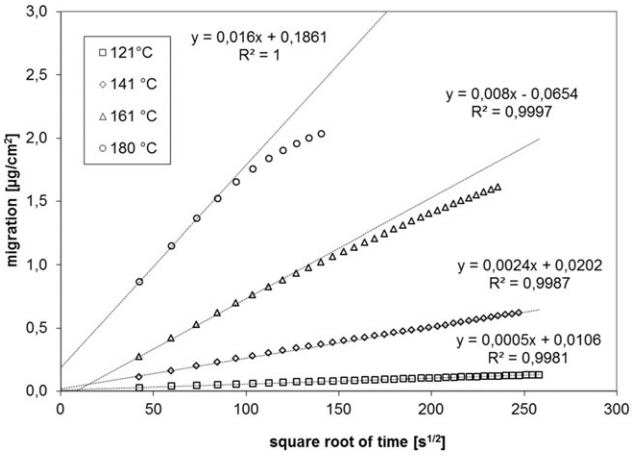

Figure 3. Migration of *n*-hexadecane from PET into the gas phase at temperatures between 120 and 179°C ($A = 7.3$ cm^2, $c_{P,0} = 125$ ppm).

Diffusion coefficients can be determined from the linear correlation between the square root of diffusion rate and the area-dependent migration according to eq. (6). Several migrants can be determined simultaneously provided the model compounds are distributed homogenously in the polymer and GC separation is attained. Therefore, we spiked the PET melt during preform production before the preforms blown to PET bottles. Notably, a proportion of the migrants evaporate during the thermal steps of preform manufacturing and bottle blowing. Thus, compounds of higher volatility are removed in larger amounts, leading to lower concentrations in the final spiked PET bottle. It was therefore necessary to analyze the final PET bottles according to their residual concentration of the artificially spiked compounds. Another important point to consider in this process is that the concentrations of the spiked migrants are not too high in order to avoid plasticizing effects. We used concentrations of up to 800 mg kg^{-1} for individual substances and the total amount of chemicals did not exceed 800 mg kg^{-1} (bottle A) and 2700 mg kg^{-1} (bottle B), respectively. In sample C only tetrahydrofurane was determined, which had a concentration of 8.7 ± 1.0 mg kg^{-1}. The proposed method determines the migration of migrants from PET bottle wall strips into the gas phase. Since, swelling effects of the polymer matrix by sorption of the simulants is thereby negligible, the migration is independent of the simulant and the mass transfer is affected only by the diffusion of the migrant in the polymer. Swelling effects with simulants like 50% or 95% ethanolic solutions, as reported in the literature,[5,9] typically lead to increased diffusion of the migrant in the polymer over time.

The proposed method was used to measure the migration of 13 model migrants into the gas phase in two sets of spiked bottles at temperatures between around 120 and 180°C. Examples of toluene, benzophenone, hexadecane, and tetrahydrofurane are given in Figures 1–4. The remaining investigated migrants show very similar migration curves. The migration of all investigated substances in PET follows a Fickian diffusion behavior. This is indicated by the linear function between the area-dependent migration and the square root of time up to ~60% of the total mass transfer. The diffusion coefficients can then be derived from the slopes of these linear correlations using eq. (6). The experimentally-determined diffusion coefficients for the model

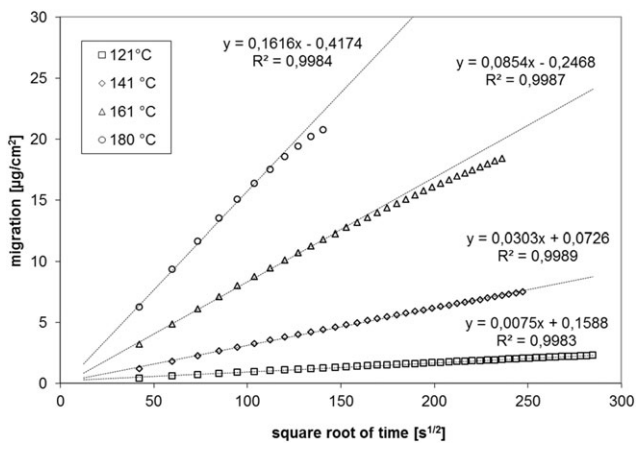

Figure 2. Migration of benzophenone from PET into the gas phase at temperatures between 121 and 180°C ($A = 7.3$ cm^2, $c_{P,0} = 786$ ppm).

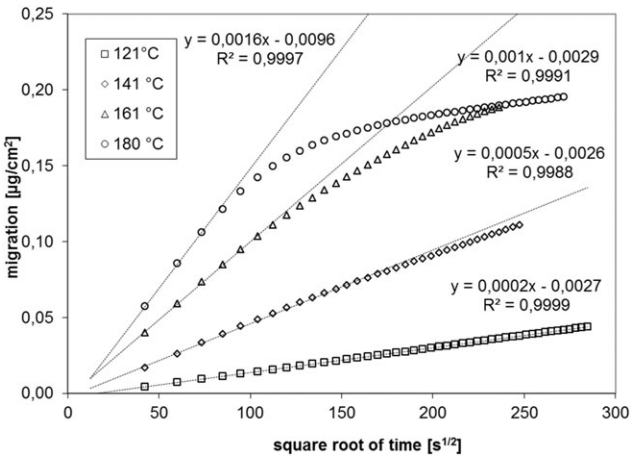

Figure 4. Migration of tetrahydrofurane from PET into the gas phase at temperatures between 121 and 180°C ($A = 7.3$ cm^2, $c_{P,0} = 8.7$ ppm).

Table II. Experimentally Determined Activation Energies of Diffusion in PET

Compound [molecular weight (g mol^{-1})]	Temperature range (°C)	Activation energy (kJ mol^{-1})	Pre-exponential factor D_0 (cm^2 s^{-1})
Tetrahydrofuran (72)	121–180	116.5	4.4×10^5
Toluene (92)	121–180	121.4	3.5×10^6
Chlorobenzene (113)	121–180	118.4	3.4×10^6
Decane (142)	120–179	145.7	2.8×10^8
Phenyl cyclohexane (162)	121–180	167.5	1.4×10^{11}
Dodecane (170)	120–179	162.2	2.6×10^{10}
Benzophenone (182)	121–180	155.4	1.8×10^{10}
Tetradecane (198)	120–179	172.8	2.8×10^{11}
Hexadecane (226)	120–179	179.2	4.5×10^{12}
Octadecane (254)	120–179	184.1	5.9×10^{13}
Eicosane (282)	120–179	190.0	7.5×10^{13}
Methyl stearate (298)	121–180	184.3	1.8×10^{13}
Docosane (310)	120–179	194.3	7.8×10^{13}

compounds in PET at four different temperatures are summarized in Table I. Tetracosane was also spiked into bottle A but could not be measured due to the very low migration of tetracosane under the applied migration conditions.

Activation energies of diffusion were calculated according to eq. (7) using the correlation of the logarithm of the diffusion coefficients versus the reciprocal temperature. The resulting activation energies E_A for all investigated model compounds are summarized in Table II. The Arrhenius plots are shown in Figures 5 and 6, demonstrate the good linearity that was found for all investigated compounds. Figure 7 shows the correlation between the molecular weight and the activation energies of diffusion determined within this study. Such a correlation is potentially useful for predicting activation energies of other molecules. However, a clear function could not be found using the data of this study. The logarithmic correlation (dashed line in Figure 7) seems to be a suitable function for such a correlation.

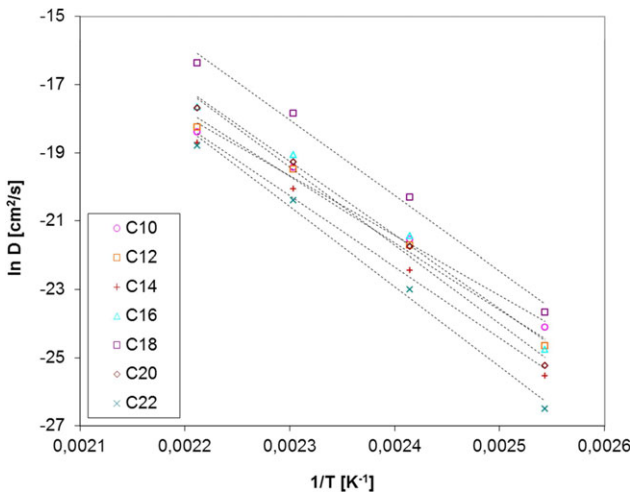

Figure 5. Arrhenius plot for the *n*-alkanes (bottle A). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Data on activation energies of diffusion for organic migrants in PET are scarcely available in the scientific literature. There are only three known publications dealing with the activation energies of diffusion of organic molecules in PET. Welle and Franz[7] reported the activation energies of acetaldehyde, benzene and tetrahydrofurane, with the values being in good agreement with the activation energies found in the present study. Diffusion coefficients for tetrahydrofurane (measured in tap water) between 23 and 50°C and values at high temperatures (this study) are available. It is interesting to note that the Arrhenius plot at low temperatures was in good agreement with the Arrhenius plot at high temperature determined in this study (Figure 8). This indicates that the diffusion behavior above or below the glass transition temperature of PET (~80°C) does not vary significantly. On the other hand, the crystallinity of the bottle wall strips (measured by differential scanning calorimetry,

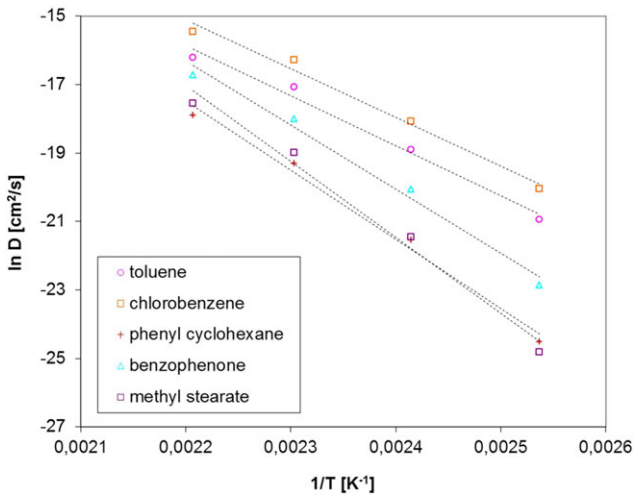

Figure 6. Arrhenius plot for toluene, chlorobenzene, phenyl cyclohexane, benzophenone, and methyl stearate (bottle B). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

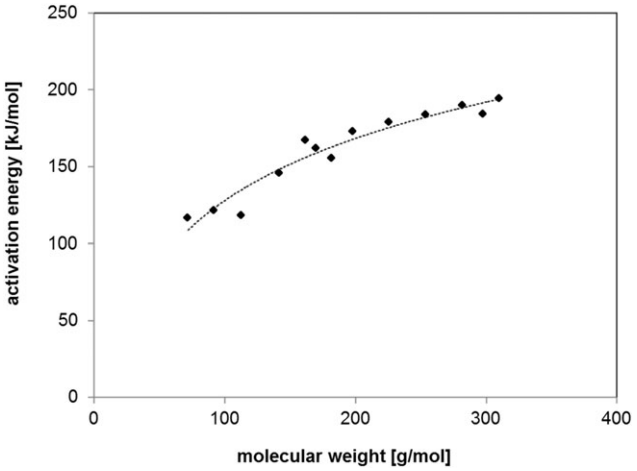

Figure 7. Correlation between the activation energies of diffusion and the molecular weight of the migrants (data from Table II).

DSC) increased from about 40% only up to about 52% after treatment at 180°C. The PET bottle wall strips were therefore presumably not completely crystallized, which explains the similar activation energies of diffusion below and above the glass transition temperature.

Pennarun et al. determined activation energies of surrogates and additives in PET[9] and reported values of between 80 kJ mol^{-1} and about 150 kJ mol^{-1} for substances in the molecular weight range of ~80 g mol^{-1} to ~200 g mol^{-1}. These activation energies were calculated from the diffusion coefficients at 40°C and 60°C. These data in general seem to be lower than those derived from our study, which reflects the fact that the diffusion coefficients at 40°C and 60°C, from which the activation energies of diffusion were derived, were determined in swollen PET. The activation energies of nonswollen PET in the present study are therefore lower. Activation energies of diffusion determined by

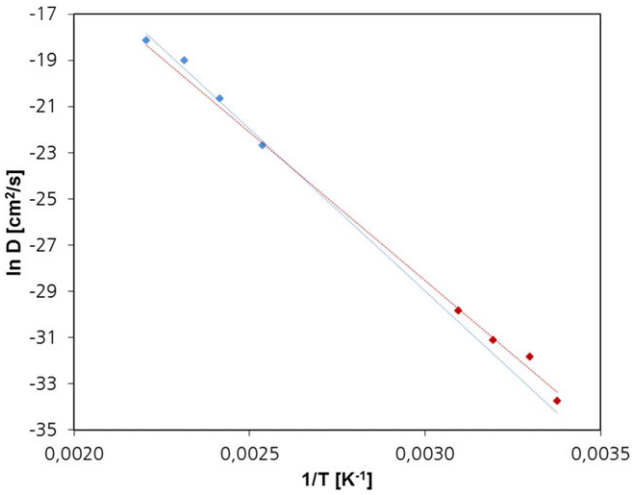

Figure 8. Arrhenius plot for tetrahydrofurane (bottle C), data from this study (red dots) in comparison to literature data (blue dots).[7] [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Pennarum et al.[9] are therefore not directly comparable to the activation energies found here. In addition, the values were calculated from diffusion coefficients within the narrow temperature range of 40°C to 60°C. If the temperature range is too small, the slope of the Arrhenius plot is susceptible to error.

Begley et al. published another set of activation energies for model compounds in PET.[10] Unfortunately, no details of the method or the simulants used are given, so it is unclear whether the activation energies were determined under swelling or nonswelling conditions. In addition, the activation energies were calculated from only two diffusion coefficient values at two different temperatures. It is therefore not clear if the Arrhenius plot results in a linear regression. The activation energies of diffusion given by Begley et al. are in several cases lower than found in our study, which additionally suggests that the diffusion coefficients were determined under swelling conditions.

CONCLUSIONS

A fast and automated method for determining activation energies of diffusion in PET (or in low diffusive polymers in general) was developed. The proposed method enables fast and precise detection of diffusion coefficients of migrants in PET at different temperatures. Furthermore, since this method is based on migration into the gas phase, swelling effects of the polymer by sorption of the food simulant is negligible. Gas-phase migration therefore provides more realistic diffusion coefficients for migrants in PET. This also results in higher activation energies of diffusion in comparison to migration tests involving swelling contact media.

The molecular weight and activation energies of diffusion of the compounds investigated in the present study were correlated. Such a correlation offers a basis for a new approach to migration modeling, as proposed in our previous study.[7] However, more data are needed to accurately predict the correlation between molecular weight (or other physical properties) and the activation energy of diffusion in the polymer. The developed method has great potential to generate the necessary dataset for refinement of the current migration model.

ACKNOWLEDGMENTS

The authors would like to thank Silvia Demiani, Anita Gruner, Alexandra Mauer, and Zuzanna Scheuerer for experimental contributions. Special thanks are due to Dr Roland Franz for fruitful discussions.

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