MEASUREMENT OF DIFFUSION COEFFICIENTS – Documentation

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Title:
Measurement of diffusion coefficients – Documentation

Abstract:
A method to measure diffusion coefficients in plastic films and coatings is described. This method is based on weighing absorbed amounts of water when conditioned samples are exposed to water or water vapour. A similar procedure based on weight loss is also possible. The same method can be also be applied to measuring diffusion coefficients of organic solvents in plastic films and coatings. The results of this project have confirmed that the use of desiccators should be limited to conditioning samples only, and not for establishing conditions for following the absorption or desorption of water, for example. Experimental results confirm the need to report the information required in the proposed Nordtest method POLY 188 “Measurement of Diffusion Coefficients”.

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**BACKGROUND – GENERAL CONSIDERATIONS**

The procedure described here allows determination of the diffusion coefficient of a gas or liquid in a polymer film. It is assumed that weight gain or loss is determined at constant temperature, but in principle any analytical technique to establish the amount of material absorbed or desorbed at the given exposure times can be used. The experimental procedure starts by conditioning the samples to equilibrium with a given environment. The samples are then placed in a new environment. The experimental procedure ends when an equilibrium uptake or loss, \( M_\infty \), is established in the new environment. Attainment of equilibrium is confirmed by no further weight change for two or more successive exposure times.

The combined effect of diffusion coefficient, \( D_o \), the film thickness of a free film that is exposed on two sides, \( L \), and the elapsed time, \( t \), is described with the dimensionless time parameter, \( T \), as follows:

\[
T = \frac{D_o t}{L^2}
\]

The customary units for \( D_o \) are \( \text{cm}^2/\text{s} \), for \( t \), s, and for \( L \), cm.

If a one-sided exposure is used, such as for a film attached to a non-absorbing substrate, one must multiply its film thickness by 2 and use this as \( L \) in the above equation.

**Constant diffusion coefficient**

Solutions to the diffusion equation for a constant diffusion coefficient can be found in the literature, and perhaps most clearly in Crank's book "The Mathematics of Diffusion" from 1956/7 (1). Useful figures are also provided where the background crosshatching allows accurate reading of data. When the uptake is one-half that of the final amount, \( M_\infty /2 \), the value of \( T \) is 0.049. It is assumed that the concentration of the absorbing material immediately reaches \( M_\infty \) just at the exposed surface. For the sake of simplicity \( M_\infty \) is often used to normalize the weight change, which thus increases from 0 at the start of the experiment to 1.0 at the end.

When the diffusion coefficient is a constant the absorption (loss) is expected to follow a straight line passing through the origin when the absorbed (lost) amount is plotted against the square root of time.

**Concentration dependence**

The same experimental procedure is also applied where concentration dependent diffusion coefficients are encountered. The diffusion coefficient measured by the method is then called an average diffusion coefficient, and additional experiments or assumptions are needed to elucidate the true diffusion coefficients (1-3). Reference is made to the literature for the procedures required (1-3). In such cases additional measurements are required where \( M_\infty \) is different for each. This can be done with water, for example, by exposing to water vapour at different vapour pressures until equilibrium is reached in each case. Some extra consideration is required if, for example, the half-time for absorption with a relative humidity change from 0% to 100% is significantly different from that for a change from 0% to 50% for the same sample (thickness). For concentration dependence the higher amount of water present in the test at the higher relative humidity should lead to a shorter half-time. On the other hand if there is a significant external resistance, the half-time for the higher relative humidity will tend to be longer since more water must be transferred to the sample. The procedure described in this Nordtest method is used for each experiment, and for these reasons, full reporting of the relevant data is required. For typical organic solvents, the local diffusion coefficient increases by a factor of about two for each additional volume percent absorbed at low concentrations.

**External and surface resistances**

The surface concentration of the sample does not increase immediately to \( M_\infty \) as assumed in the above if there are significant external or surface resistances in the absorption (or desorption) experiment. External resistance can come from long pathways of diffusion of water in air, from
heat transfer requirements to allow for evaporation (or condensation) of water, or from effects just at the surface of the sample. The experiments performed in connection with this project confirm that ordinary laboratory desiccators, for example, should not be used for anything other than establishing an initial equilibrium condition. The uptake or loss measurements must be made under conditions that maintain a constant climate. It is suggested that the weight uptake or loss measurements be made in a (larger) climatized room. If desiccators or similar containers are used then proof must be supplied that the reported climate remains constant and does not change during the course of the experiment. It has been shown here that the climate in desiccators is not constant during typical absorption and desorption experiments of the kind described. Significant time elapses until the expected equilibrium is re-established every time the lid is removed. Diffusion of water in air can easily be a significant resistance factor in these closed spaces as well.

If there is an external or surface resistance, it will clearly become more important as the film thickness decreases. The diffusion coefficient measured by this Nordtest method should be the same regardless of film thickness. The effect of a significant external or surface resistance is that the experiment takes longer than otherwise expected and the apparent diffusion coefficient will be too low. The uptake (loss) curve is delayed and the linear portion of the curve does not pass through the origin. This is sometimes referred to as an “S-shaped” curve in the general literature.

The example cited in the previous section for the absorption of water from 0% relative humidity to either 50% relative humidity or to 100% relative humidity is repeated here for the sake of completeness. If the half-time for the test at the higher relative humidity is significantly longer than that for the lower relative humidity test, then one can suspect an external resistance. The amount of water being transferred is larger and this amount can simply not reach the sample and be absorbed in the same period of time as the smaller amount being transferred in the lower relative humidity test. In desorption experiments the loss of water is retarded since the concentration of water in the air is not zero as expected but varies from zero at the desiccant surface to a higher value at the sample surface. One must eliminate the source of the external resistance or extend the studies to fully account for the external resistance in a satisfactory manner.

The assumptions on which this Nordtest method is based are not fulfilled if the sample being tested allows water to collect into “clusters” at higher humidity. This can be strongly suspected if the sample contains hydrophilic components and if the equilibrium uptake at say 50% relative humidity is far less than that at 100% relative humidity. Such an example is presented in the experimental section that follows.

Surface and external resistances in the measurement of diffusion coefficients and permeation coefficients in polymers are discussed in the documentation that follows as well as in several other reports (4-7).
PROCEDURE

Preliminary Preparation
The samples must be conditioned so the initial state of the sample is constant and well defined before starting the experiment itself. This is not always easy for studies that measure diffusion coefficients for water, however, since the water content of ordinary air can vary rapidly, and the water content of samples will increase or decrease accordingly. Water contents must be known in a diffusion experiment, since significant amounts of absorbed water can influence the diffusion of water itself, and also the diffusion of other chemicals as well. Absorbed water acts like a plasticizer. Conditioning to the equilibrium value in climatized air can require several weeks at room temperature. The time required to reach equilibrium depends on the diffusion coefficient in the material, which, of course, is not usually known at this stage unless there is prior experience.

In rigidly correct studies, it is necessary that the local concentration of water in the sample is uniform throughout the sample thickness. This must be confirmed. One can start with essentially no water in the sample by storing it over a fresh desiccant in a closed container. The length of time required before all the water is removed must be determined by weighing to constant weight or storing for a predetermined time that assures the equilibrium condition. The experiment then starts by removing the sample from the dry climate and weighing it in a constant temperature and constant humidity climate, such as in a climatized room. Samples can also be stored until equilibrium absorption is attained over water, or over a salt solution that provides constant humidity, in which case an intermediate water uptake will be achieved. The experiment starts when the sample is removed from the conditioning chamber and weighed in a constant temperature and constant humidity room.

As discussed above, diffusion coefficients can also be found from desorption measurements using essentially the reverse of the process described here. The half-time used is that for one-half of the initial amount of diffusing material to be desorbed to the air in a climatized room.

It is emphasized that the use of desiccators is not recommended for anything but establishing an initial equilibrium condition. A sufficiently large climatized room is required to do the actual study. Proof of sufficiently constant conditions for the absorption and/or desorption studies must be provided.

The initial uniform distribution of water in the sample is attained when the weight no longer changes at the given condition. The required time will vary with film thickness, temperature, and, in fact, the diffusion coefficient to be measured as stated above. In some instances, one must perform the measurements according to best judgement. This means establishing the probable diffusion coefficient/time required to change the amount of water in the sample from one (equilibrium state) condition to another (equilibrium state) condition, and then compare that this time was indeed shorter than the equilibration time used to condition the sample.

If a diffusion coefficient is known or can be estimated, it can be used to calculate required conditioning times for films with different thicknesses. Changing from one equilibrium state to another requires that the dimensionless time, $T$, is equal to about 0.4, when the thickness is defined as above. The film thickness affects the time required for the conditioning process where it enters as its square, so changes in film thickness have a very large effect on diffusion phenomena.

Measurements
A laboratory work sheet is helpful to record and interpret the data required to determine diffusion coefficients. The data required are weight gain (or loss) as a function of exposure time. Experiments can last for weeks or months. Errors can arise in weighing small amounts of absorbed material when the exposures have been in liquid water, for example. Systematic and reproducible removal of excess surface water with tissue or cotton in a reasonably rapid manner is essential when water absorption is to be determined. This procedure is generally acceptable since diffusion of water to a surface where it can evaporate is usually much slower than the evaporation process itself.
Total removal of surface water has higher priority than speed of removal. The errors from weighing excess surface water are expected to be much larger than errors caused by careful but slightly slower handling prior to actual weighing. The drying of surface water should be done uniformly each time such that the time used is approximately the same at each time interval. Variations in handling the samples should be avoided.

In any event the required data are weight gain (or loss) with time. Suggested time intervals for the weighing are as soon as possible at the start of an experiment followed by time intervals that are the double of the time of the prior measurement time. An example might be 0, 1 hour, 2 hours, 4 hours, 8 hours, 1 day, 2 days, 4 days, 8 days, etc. If the films are thin and diffusion is rapid the “hours” in the previous example must be replaced with “minutes” with subsequent times chosen to provide a usable absorption (desorption) curve. It is suggested that a plot of weight gain or loss versus the square root of time be made and followed during the course of the experiments. This allows better control of the experiment. The time intervals can be shortened or lengthened, and one can see whether the absorption curve is starting to bend toward the equilibrium value.

**Calculations**

The data are plotted as weight gain (loss) versus the square root of the exposure time. It is expected that this plot will result in a straight line passing through the origin that finally flattens out as it approaches the equilibrium absorption (loss) condition. When the equilibrium amount, \( M_{\infty} \), is finally established, one divides this value by 2 to find \( M_{\infty}/2 \). The square root of the half-time for equilibrium absorption (desorption), \( (t_{1/2})^{1/2} \), is read from the curve by noting the value required for the change in weight to equal \( M_{\infty}/2 \). This value is then squared to find \( t_{1/2} \). The diffusion coefficient where \( L \) is the thickness of a free film exposed on two sides is then found from

\[
D_o = .049 \frac{(L^2)}{(t_{1/2})} \text{ cm}^2/\text{s}
\]

If a one-sided exposure is used, such as for a film attached to a non-absorbing substrate, one must multiply its film thickness by 2 and use this as \( L \) in the above equation.
DISCUSSION

Values for the diffusion coefficient of water in most barrier polymers are in the range of $10^{-8}$ cm$^2$/s or lower. The values for diffusion coefficients for organic solvents in these same polymers can vary greatly, but one can start with estimates near $10^{-11}$ cm$^2$/s at room temperature. Larger molecular weight species have still lower diffusion coefficients. The diffusion coefficient can be expected to approximately double with a 10°C increase in temperature.

If a product is being tested, then the sample should be chosen to reflect something characteristic for the product, if possible, to avoid unnecessary extrapolations. The thickness of the sample should be one found on the product, for example. If this poses a problem, then one can beneficially choose thinner samples based on the time-to-equilibrium requirement. The requirement for reasonably accurate weighing may indicate thicker samples. Somewhere between these is an optimum.
SPECIAL CASES

Film thickness effects and external resistances

If there is an effect of film thickness on the observed diffusion coefficient, this is then called the apparent diffusion coefficient, \( D_{\text{app}} \). The true diffusion coefficient, \( D_{\text{true}} (D_0) \), can be found by extrapolation of a plot of \( 1/D_{\text{app}} \) versus \( 1/L \) to zero. This extrapolation eliminates external and surface effects since these lose their importance at infinite film thickness. The following equations show why this plot is useful.

\[
F = \frac{\Delta c}{(L/D_{\text{app}})} = \frac{\Delta c}{(L/D_{\text{true}} + R_1 + R_2 + R_3 \ldots)}
\]

\[
L/D_{\text{app}} = L/D_{\text{true}} + R_1 + R_2 + R_3 \ldots
\]

\[
1/D_{\text{app}} = 1/D_{\text{true}} + (R_1 + R_2 + R_3 \ldots)/L
\]

\( F \) is the flux and the driving force for the diffusion process is \( \Delta c \). The various “\( R \)” are external or surface resistances as described elsewhere.

The procedure given in the Nordtest method must be repeated for films of different thickness for this type of study. Care must be taken to make certain that the films are as identical in properties as possible for such a study. This is very difficult if not impossible to ensure when solvent-based coatings are being studied. More and more solvent is retained as the film thickness increases, and this causes a misleading result since the diffusion coefficients will tend to be higher as film thickness increases.

End effects

End effects can become important. Diffusion coefficients measured using, for example, tensile testing bars certainly require correction. For this reason the use of such samples in not recommended. The following equations can be used to estimate the consequences of potential end effects and to correct for them if there is no alternative. These equations are derived from the initial rates of uptake (or loss), so that these should be used to extrapolate to a half-time for the given experiment.

For plane geometry:

\[
D_0 = \frac{D_{\text{app}}}{(1 + L/l + L/w)^2}
\]

The length of the plane sample is given by \( l \) and its width by \( w \). \( L \) is retained as the film thickness.

For cylindrical geometry:

\[
D_0 = \frac{D_{\text{app}}}{(1 + L/R)^2}
\]

The radius of the cylinder is \( R \), and \( L \) is again retained as the sample thickness.
EXPERIMENTAL DOCUMENTATION

Introduction
The purpose of this experimental documentation is to show why the different requirements for information in the proposed Nordtest method called “Measurement of Diffusion Coefficients” are indeed required. This Nordtest project has been based on cooperation between FORCE Technology (FORCE) as project leader, with Tenna Brandt Nielsen, Nanna Svendsen and Lisbeth Just taking part, and the Swedish National Testing and Research Institute (SP), where Kenneth Möller was responsible. Both parties have measured the films of the same materials for the purpose of comparisons between laboratories. There has been considerable discussion and experimental activity associated with the use of desiccators, a practice that is very common for this type of measurement.

Experimental
The following experimental procedures and conditions were used at FORCE Technology:

Equipment:
5 different paints
Aluminium plates 9 x 15 cm, thickness 1mm
3 desiccators (size 26 cm diameter and 24 cm high, containing water / silica gel / saturated Magnesium nitrite (RH 54.3%).
Climatised room 20° RH 50% ± 1%.
Applicator Sheen, gap 120 µm.
Detergent ABC-Clean, ABC-Clean Engineering A/S.
Mitutoyo Thickness gauge (0.001 mm)
Electronic scale, Mettler-Toledo B6 series no. 15665

Four plates were used for each paint - two were dehydrated at RH 0% and two were humidified at RH 100%.
The aluminium plates were cleaned in detergent, and then rinsed in de-ionised water and acetone.
The dry plates were weighed and the paints were applied using an applicator with a suitable gap. The required film thickness was thought to be ≥ 100 µm in order to ensure that the uptake would not be too small. The paints were applied at a thickness and with a drying procedure recommended by the supplier.
All of the samples were made by FORCE Technology and half of them were sent to Kenneth Möller, Swedish National Testing and Research Institute, including data for tare weights and results of thickness measurements.
The film thickness was measured 6 times at different places by taking a total sample thickness and subtracting the film thickness of the aluminium plate. The average value was used. The plates were placed in a climatized room at 20°C in desiccators containing water RH 100% or a desiccant (Silica gel) RH 0%. They were weighed until constant weight was achieved.
The plates were then placed in desiccators containing Mg(NO3) to attain a relative humidity of 54.3% at 20°C in the laboratory (series 1) or in a climatized room 20°C RH 50% ±1% (series 2).
The weight change was measured and the time recorded until equilibrium was attained. The weight changes are given relative to the fully dried or moistened weight.
The weight change was plotted against the square root time.

The following experimental procedures and equipment were used at SP:

20 litre desiccators were used. The desiccators were filled with silica gel or saturated solutions of (Ca(NO3)2 4H2O) from Riedel-deHaen. Purity > 99 %.
The desiccators were kept in a Weiss Technik WK 111 climatic cabinet at 20 +/-0.2 C. The situation was a little bit strange, since it probably would have been better to expose the samples outside the desiccator (in the climatic cabinet).
The balance used was a Mettler Toledo AT201. Maximum weight 205 g. Accuracy: 0.00000+/−0.00002 g.
The relative humidity was measured using a Rotronic Hygromer AM3 instrument and Rotronic MP101A RH probe.
Film thickness values were supplied by FORCE Technology (Tenna Brandt Nielsen): The thickness of the EPDM rubber was 2.5 mm.

**Results with desiccators as test chambers**
There is no question about the use of smaller enclosed vessels such as desiccators for the conditioning of samples. They can be supplied with water, fresh desiccant, or salt solutions having various concentrations, such that a wide variety of experimental environments can be established and maintained. The experiments reported in Figure 1 (SP), however, clearly lead to the conclusion that these are not well suited for use as chambers at the same degree of constancy as a larger climatized room will supply. The magnitude of the errors introduced by this effect depends on the given situation. This effect will be more important for the experiments where the time to equilibrium is comparable in duration, of course, and it may even be negligible where very long experimental times are involved. Results given below show that removing the lid also disturbs the climate being sought within the desiccator.

![RH versus time during drying](image)

*Figure 1 shows response time after putting the lid onto a desiccator filled with silica gel. There are no samples in the chamber. The relative humidity falls uniformly to essentially zero after a period of 40-50 minutes. The first curve in the figure is the response time of the relative humidity detector. The final curve measures the effect of taking off the lid. Such a chamber can not be recommended for use whenever 40-50 minutes is significant in terms of an experiment where the surface concentration is assumed to immediately fall to essentially zero in the case. The diffusion coefficients will be perceived as being too low since the experiment takes longer than it should based on the assumptions.*

In spite of the above, and for the sake of comparison, many measurements were made at SP and at FORCE in this type of chamber. These data from SP are reported in the following set of figures and in Table 1. These figures are collectively called Figure 2, and report both water uptake and water loss as a function of time as well as a function of the square root of time, as recommended in the proposed Nordtest method. In addition the evaluations include a comparison with what is
expected from the appropriate solution to the diffusion equation (Theory), as reported in Crank (1975, Equation 4.18), where the surface concentration increases immediately to $M_\infty$. A straight-line relation using the square root of time as discussed in the General Considerations is confirmed in all cases. These data would lead one to believe that the surface concentration was indeed relatively constant. The absolute magnitude of $M_\infty$ will not affect $D_0$, and does not enter into the calculations or interpretations unless there is concentration dependent diffusion or other factors not in agreement with the assumptions. See also the discussion in the General Considerations section related to this effect.

The corresponding figures for the studies at FORCE are not included for the sake of keeping the report acceptable in length.

Diffusion coefficient measurements were done for both water uptake and water release for the types of films listed below. The coatings were applied to aluminum substrates at FORCE. Half of them were then sent to SP for comparison. The EPDM was tested as a free film having exposure on both sides. The film thickness values of the coatings in microns are given in parenthesis. The order is the same as the sample numbers used.

1) Solvent-borne clearcoat (156, 163, 189, 208, 148, 170, 187, 186)
2) Water-borne clearcoat (158, 171, 162, 169, 183, 129, 166, 144)
3) Hempadur 45148-13 (Hempel Marine Paints, Denmark) (79, 102, 57, 76, 90, 93, 90, 87)
4) Jotun hard top (Jotun, Norway) (240, 139, 156, 176, 213, 155, 168, 165)
5) Dyrup base 10 (Dyrup, Denmark) (101, 122, 93, 86, 94, 92, 126, 99)
6) EPDM rubber (2.5 mm)

The following are the uptake and loss results from SP in the initial studies:
Water uptake solvent borne clearcoat

Sample 5, 2K solvent borne clearcoat

Sample 6, 2K solvent borne clearcoat

Sample 7, 2K solvent borne clearcoat

Sample 8, 2K solvent borne clearcoat

Experimental data used for straight line fit

Experimental data

Theory

Experimental

Experimental data

Experimental data used for straight line fit

Experimental data

Experimental data

Experimental data
Water uptake water borne clearcoat

Sample 9, 1K water borne clearcoat

\[ y = 0.34749x \]

Sample 10, 1K water borne clearcoat

\[ y = 0.32971x \]

Sample 11, 1K water borne clearcoat

\[ y = 0.33603x \]

Sample 12, 1K water borne clearcoat

\[ y = 0.33705x \]
Water uptake Hempadur 45148-13

Sample 21, Hempadur 45148-13

\[ y = 0.25509x \]

Sample 22, Hempadur 45148-13

\[ y = 0.21491x \]

Sample 23, Hempadur 45148-13

\[ y = 0.25611x \]

Sample 24, Hempadur 45148-13

\[ y = 0.24132x \]
Water uptake Jotun hard top

Sample 25, Jotun hard top blue

Sample 25, Jotun hard top blue

Sample 26, Jotun hard top blue

Sample 26, Jotun hard top blue

Sample 27, Jotun hard top blue

Sample 27, Jotun hard top blue

Sample 28, Jotun hard top blue

Sample 28, Jotun hard top blue

Experimental data

Experimental data for straight line fit

Experimental data

Experimental data for straight line fit

Experimental data

Experimental data for straight line fit

Experimental data

Experimental data for straight line fit

Experimental data

Experimental data for straight line fit

$y = 0.20428x$

$y = 0.27578x$

$y = 0.26638x$

$y = 0.24896x$
Water uptake Dyrup base 10

Experimental data used for straight line fit

Sample 37, Dyrup base 10

\[ y = 0.67262x \]

\[ M(t)/M(t=\infty) \]

Sample 38, Dyrup base 10

\[ y = 0.67996x \]

\[ M(t)/M(t=\infty) \]

Sample 39, Dyrup base 10

\[ y = 0.58084x \]

\[ M(t)/M(t=\infty) \]

Sample 40, Dyrup base 10

\[ y = 0.75011x \]

\[ M(t)/M(t=\infty) \]
Water uptake EPDM rubber

Sample 51, EPDM rubber

\[ y = 0.05843x \]

Sample 52, EPDM rubber

\[ y = 0.05656x \]

Sample 53, EPDM rubber

\[ y = 0.05386x \]

Sample 54, EPDM rubber

\[ y = 0.05231x \]
Water loss solvent borne clearcoat

Sample 5, 2K solvent borne clearcoat

\[ y = -0.41115x + 1.00000 \]

Sample 6, 2K solvent borne clearcoat

\[ y = -0.36914x + 1.00000 \]

Sample 7, 2K solvent borne clearcoat

\[ y = -0.33860x + 1.00000 \]

Sample 8, 2K solvent borne clearcoat

\[ y = -0.32399x + 1.00000 \]
Water loss water borne clearcoat

Sample 9, 1K water borne clearcoat

Sample 9, 1K water borne clearcoat

Sample 10, 1K water borne clearcoat

Sample 10, 1K water borne clearcoat

Sample 11, 1K water borne clearcoat

Sample 11, 1K water borne clearcoat

Sample 12, 1K water borne clearcoat

Sample 12, 1K water borne clearcoat

Experimental data
Experimental data used for straight line fit

Experimental data
Experimental data used for straight line fit

Experimental data
Experimental data used for straight line fit

Experimental data
Experimental data used for straight line fit

\[ y = \text{Experimental data} \]

\[ y = \text{Experimental data used for straight line fit} \]

\[ y = \text{Experimental data} \]

\[ y = \text{Experimental data used for straight line fit} \]
Water loss Hempadur 45148-13

Sample 21, Hempadur 45148-13
\[ y = -0.25539x + 1.00000 \]

Sample 22, Hempadur 45148-13
\[ y = -0.22157x + 1.00000 \]

Sample 23, Hempadur 45148-13
\[ y = -0.23104x + 1.00000 \]

Sample 24, Hempadur 45148-13
\[ y = -0.25574x + 1.00000 \]
Water loss Jotun hard top

Sample 25, Jotun hard top blue

\[ y = -0.15387x + 1.00000 \]

Experimental data
Experimental data used for straight line fit

Sample 26, Jotun hard top blue

\[ y = -0.21674x + 1.00000 \]

Experimental data
Experimental data used for straight line fit

Sample 27, Jotun hard top blue

\[ y = -0.21950x + 1.00000 \]

Experimental data
Experimental data used for straight line fit

Sample 28, Jotun hard top blue

\[ y = -0.21329x + 1.00000 \]

Experimental data
Experimental data used for straight line fit
Water loss Dyrup base 10

Sample 37, Dyrup base 10

\[ y = -0.56684x + 1.00000 \]

Sample 38, Dyrup base 10

\[ y = -0.50144x + 1.00000 \]

Sample 39, Dyrup base 10

\[ y = -0.45469x + 1.00000 \]

Sample 40, Dyrup base 10

\[ y = -0.58369x + 1.00000 \]
Water loss EPDM rubber

Figure 2: Experimental absorption and desorption curves measured at SP.
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Table 1. Diffusion coefficient results from SP in m²/s comparing curve fitting with the half-time method and including standard deviations.

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<tr>
<td>%</td>
<td>17.76%</td>
<td>18.42%</td>
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<td>12.33%</td>
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<td>52</td>
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<td>1.23E-12</td>
</tr>
<tr>
<td>Mean</td>
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<td>1.04E-12</td>
<td>Mean</td>
<td>1.05E-12</td>
<td>1.11E-12</td>
</tr>
<tr>
<td>STD</td>
<td>1.03E-13</td>
<td>1.00E-13</td>
<td>STD</td>
<td>9.94E-14</td>
<td>1.52E-13</td>
</tr>
<tr>
<td>%</td>
<td>9.97%</td>
<td>9.63%</td>
<td>%</td>
<td>9.47%</td>
<td>13.70%</td>
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</table>

Table 2: Comparison of first round averaged diffusion coefficients measured in desiccators at SP and at FORCE. Diffusion coefficients based on half-times are reported in cm²/s. \( M_\infty \) is given in parenthesis from results at FORCE. Uptake was from 0% RH to 54.4% RH established by a salt solution in the desiccator. Loss was from saturation at 100% RH to 54.4% RH established by a salt solution in the desiccator. For the sake of comparison the EPDM sample gained 0.33% during the uptake experiment and lost 1.50% during the weight loss experiment. The total solubility at saturation is the sum of the uptake and loss values in all of these cases.

Additional studies of the use of desiccators for the purpose of measuring diffusion coefficients were also done. A comparison was made between different types of bottom plates, for example, as shown in Figures 3 and 4. The relative humidity over a salt solution drops from 50% to about 47% when the lid is removed, and then rises again to 50% after about 400 minutes for a steel net as bottom plate and after just over 600 minutes for the customary ceramic bottom plate.
Figure 3. The desiccator should maintain a relative humidity of 50% immediately after the lid is put on.

Figure 4: Shows what happens after opening the desiccator that should maintain 50% relative humidity at all times. The initial relative humidity in the figure is that of the laboratory air or about 29%. As can be seen in the figure the relative humidity has risen to about 47% after one hour. The average value during this time is 37% instead of the expected 50% during the whole period. The desiccator was empty for this experiment. If there is a sample present that is taking up water at the same time, then the delay to reach the expected 50% will be still longer.

A new water uptake experiment using the solvent borne clear coat samples was done at SP. The desiccator was in a room where the relative humidity was quite low, about 23%. The relative humidity inside the desiccator was also measured throughout the whole exposure. The
results are given in Figure 5. It can be seen that the resulting values for the diffusion coefficients are considerably lower compared to the values found when the desiccator was loaded at 50 % RH.

The weight increase of sample 6 is also shown in detail together with the change in RH during the exposure, in Figure 5. During the first 5 hours the desiccator was opened and closed at 23 % RH every hour. The weight of the samples was determined every time. The RH in the desiccator varies between 23 and 40 %. The plot of the weight gain data seems to follow a curve that asymptotically approaches the 0.6 level in the diagram. 0.6 means the 60 % level of the maximum weight gain at 50 % RH. After 4 hours the desiccator was loaded in a climatized room at 50 % RH. By introducing dry air the RH was lowered to about 40 %, i.e. to the same level as prior to opening of the desiccator. After 5 hours of exposure there was a more pronounced increase in weight than during previous exposure times. After 5 hours the desiccator was loaded in the dry room, i.e., the RH in the desiccator was 23 %. As can be seen in Figure 5, there is a weight loss between 5 and 6 hours (for all four samples). After 6 hours the starting level inside the desiccator was once again 40 % resulting in a considerable weight increase between 6 and 7 hours. The starting humidity level after 7 hours was 23 % leading to a considerable weight loss between 7 and 8 hours (once again for all four samples). No measurements were done between 8 and 15 hours leading to a relative weight increase almost up to 100 %. To summarize the discussion above: if the RH level is not kept constant during an exposure the result will be incorrect values for the diffusion coefficients.

The calculated results of these experiments are given in the last entries in Table 3. $D_0$ is given in m$^2$/s. The solvent-borne clearcoat was measured on two different occasions using both a net at the bottom of the desiccator as well as the customary ceramic plate. The results in both cases were the same as can be seen from the results reported in Table 3, where all of these diffusion coefficient measurements are summarized. The same result was also found in the initial experiments. There is a high degree of repeatability in these experiments in spite of the uncertainties associated with the relative humidity in the desiccator.

The diffusion coefficients based on the curve fitting procedure are (statistically) the same as those based on the half-time equation, so the comparisons in the following will use the latter. This is also the procedure described in the proposed Nordtest method.
Solvent borne clearcoat, Water uptake using metal net as desiccator bottom plate

<table>
<thead>
<tr>
<th>Sample</th>
<th>Curve fit</th>
<th>( t_{1/2} )</th>
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<td>STD</td>
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</tr>
<tr>
<td>%</td>
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</table>

Table 3. Diffusion coefficients in m²/s for the solvent borne clear coat for various conditions in the desiccator.

Water uptake using ceramic plate as desiccator bottom plate
Desiccator loaded in a room at 23 % RH

<table>
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<tr>
<td>%</td>
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<td>13.46%</td>
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</table>

Table 4. Comparison of diffusion coefficients measured at FORCE (climatized room and desiccator in dark type) and at SP (simulated climatized room).

Results of studies in a climatized room

A final comparison was made between measurements where conditioning was done in a desiccator and actual weight change took place in a climatized room. This comparison of diffusion coefficients measured at FORCE in a climatized room with those measured at SP in a desiccator simulating a climatized room are given in Table 4.
DISCUSSION

The results given in Table 1 allow an estimate of the magnitude of potential errors in the diffusion coefficient measurements since standard deviations are also reported. The standard deviations using 4 different measurements for each sample can be as high as 18% with the lowest being 4.71%. Many are greater than 10%, and 10% to 15% appears to be what can be expected from the experiments themselves at a given laboratory on the same sample films. Errors in film thickness measurement are in addition to this. These errors often have an order of magnitude of 10%. The square of the film thickness is used in the calculations. There was considerable variation in the film thickness of some of the coatings, as reported in the above.

The averaged $D_0$ for a given material found from absorption and desorption were all within approximately two standard deviations using the value for the type of experiment giving the largest standard deviation. They can therefore be considered as being in reasonably good agreement with each other. A closer analysis of differences may be possible if the variation of relative humidity in the desiccator is considered, but this is judged beyond the scope of this project.

An examination of the times required to attain equilibrium change suggests that 48 hours of conditioning is sufficient for most of the coatings studied in this project. An exception is the Jotun hardtop where conditioning for 3-4 days is required, as can be seen from the desorption data. The Dyrup coating has reached equilibrium within 8 hours, so there are variations. These depend on $D_0$, of course, as discussed in the General Considerations in more detail. These conditioning times would also account for the lag-time in the desiccator itself, since this is, in effect, also built into the experiments. The error associated with the lag-time to reach equilibrium conditions within the desiccator is less significant for the materials requiring the longer experimental times, as discussed above. The longest conditioning time required in this study is for the EPDM rubber. A time of about 800 hours is required, not because of a low $D_0$, but because of the greater film thickness.

The EPDM has the highest diffusion coefficient, which might have been expected since elastomers are more flexible than harder coatings. This polymer chain segment mobility enhances the diffusion of smaller molecules.

The results reported in the above confirm that desiccators should only be used for conditioning of samples. The effects of the external climate on the results can not be predicted. Experiments that start with zero water content and rise with absorption to some equilibrium value will be delayed if the relative humidity of the outside air is lower than that sought for in the desiccator. In other words 50% relative humidity in the outside air will slow attainment of equilibrium at 100% relative humidity within the desiccator. Similar delays in desorption experiments will also be encountered. If a water-saturated sample is placed in a desiccator at 0% relative humidity, opening the lid will allow air from the laboratory to enter. This will carry some water with it, and this must also be ultimately removed on toward the end of the experiment. It may be possible that opening the lid can actually hasten the process if water vapor diffusion in the air within the desiccator is slow relative to the rate at which water can actually leave the film. In this case, especially at the start of experiments, the opening of the lid at lower relative humidity in the laboratory air may actually help remove water from the sample. The answer to these problems is clearly to use desiccators for conditioning and not for the absorption or desorption tests. The samples should not be removed from the climate at which the test is being made. This is further confirmed in the data in Figures 3-5 and in Table 3.

Table 2 compares SP and FORCE data for averaged diffusion coefficients where both used desiccators. It can be seen that absorption and desorption experiments at FORCE gave results that differ by a factor of about 4 for the first two coatings. Depending on which comparisons are made, there are several differences between the partners that are between factors of 2 to just over 3 for the same coatings. The diffusion coefficient for the Hempadur 45148-13 coating is the lowest in the study, and this is probably why the agreement is so good, no matter how one makes a comparison. Even here though, the desorption data differ by 40%. The Jotun Hard
Top coating has a slightly higher diffusion coefficient, and the differences are larger than for the Hempel coating. The differences can be about 50%. The Dyrup Base 10 is perhaps a little special, as discussed below.

The data from FORCE in Table 4 resulted from removing conditioned samples from desiccators at either 0% relative humidity or 100% relative humidity, and then weighing them in a climatized room at 20°C and 50% relative humidity. This procedure significantly reduced the differences between the diffusion coefficients measured by absorption and desorption, respectively. The data point from SP, where an attempt was made to simulate these climatized room conditions using a desiccator, gave a result that is essentially the average of the absorption and desorption results found at FORCE for the given coating. There are still what would normally be considered significant differences between the diffusion coefficients found by absorption and those found by desorption, even in a climatized room. It appears that one must accept differences in the range of 50% in most cases, but in isolated situations a difference by a factor of 2 or even 3 is what can be anticipated. In the present study a difference of a factor of 2.8 was found for the Dyrup Base 10 coating. It is thought that this originates from the large amount of water in the samples conditioned at 100% relative humidity. These films contained 90 mg/g water at saturation (or supersaturation) and only 4 mg/g at approximately 50% relative humidity. Some coatings of this type contain hydrophilic components that collect water at high relative humidity to such an extent that water clusters into separate regions and even blisters can be formed. When this happens, the primary assumptions are no longer valid, and the results can not be considered within the scope of the method described in the General Considerations section above. The fact that all of the desorption results are relatively close and lower than the absorption results could support the slowing down of the water loss by a mechanism at least partly controlled by surface evaporation (or disappearance of clusters) rather than by diffusion alone. High water content could also lead to concentration dependent diffusion, but one would then expect faster transport at higher water concentrations, and this is not the case.
SUMMARY

The documentation has confirmed that desiccators should only be used for conditioning samples. The weight gain or weight loss tests should be performed in a suitably large climatized room such that the experiments themselves do not interfere with the proper functioning of the room. Samples should not be removed from the conditioned environment during testing. Because of the extra variability caused by the desiccators in most of the studies, it has not been possible to arrive at a reliable prediction of the variation expected in this type of study. It can be seen, however, that studies of absorption and desorption on the same coatings can yield diffusion coefficients that vary by a factor of four in isolated cases. Differences by factors of two are not unusual, and differences in the range of 50% should be anticipated even in the best of studies.

REFERENCES


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