16 Absorption and Diffusion in Polymers

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ABSTRACT

Predicting whether or not a given chemical will attack a given polymer is important. Hansen solubility parameters (HSP) have been used for this purpose as discussed elsewhere in this book. Consideration of the absorption and diffusion of the chemical in the polymer is often required in addition to HSP in order to make reliable predictions, however. This has been discussed in particular in Chapter 12 through Chapter 14, where chemical resistance, barrier properties, and environmental stress cracking are treated in detail. Chemicals with smaller and more linear molecules absorb and diffuse more readily than those with larger and more bulky structures. Surface resistance to absorption is sometimes so dominating that absorption does not occur in some cases, even though this might be expected based on simple HSP considerations. This chapter examines surface resistances in connection with absorption and diffusion in polymers in order to help improve understanding of these factors and to emphasize the necessity of simultaneous consideration of surface resistance when absorption rates and diffusion within the bulk of the polymer itself are of interest. Methods to measure surface resistance and concentration-dependent diffusion coefficients are discussed. Solving the diffusion equation with simultaneous consideration of surface resistance and with a concentration dependent diffusion correctly models absorption, desorption, film formation by solvent evaporation, and various forms of so-called anomalous diffusion such as "time-dependent," Case II, and Super Case II. Surface phenomena such as surface resistance to absorption deserve far more attention than has been given in the past.

LIST OF SYMBOLS USED IN THIS CHAPTER

(Please note that these are different from those used in the other chapters.)

A	Minimum cross-sectional area of molecule in Equation 16.20
B	Ratio of diffusion resistance to surface resistance. See Equation 16.13
C	Dimensionless concentration. See Equation 16.5
C_A	Concentration at break in curve in Figure 16.1
C_s	Dimensionless surface concentration
D	Diffusion coefficient. Preferred units are cm^2/s
D_0	Diffusion coefficient at zero concentration or lowest concentration in an experiment
D_1	Diffusion coefficient on exposed side of film
D_2	Diffusion coefficient on exit side of film
D_{app}	Apparent diffusion coefficient
D_{av}	Average diffusion coefficient
D_{max}	Maximum diffusion coefficient in an experiment
D_v	Increase in the diffusion coefficient over zero conditions for a given situation
F	Mass flux
F_M	Correction factor for concentration dependent diffusion in Equation 16.11
F_B	Correction factor for surface resistance in Equation 16.11
F_a	Correction factor for concentration dependent diffusion in absorption experiments

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F_d	Correction factor for concentration dependent diffusion in desorption experiments
L	Film thickness
M_t	Absorbed mass at time t
M_∞	Mass at equilibrium conditions
P	Permeation coefficient
P_{app}	Apparent permeation coefficient
P_∞	True permeation coefficient
R	Radius of cylindrical sample in Equation 16.24
R_d	Resistance to mass transport from diffusion
R_i	Resistances to permeation from sources 1, 2, 3, etc., in Equation 16.17 to 16.19
R_s	Resistance to mass transport by surface resistance(s)
T	Dimensionless time given by Equation 16.3
X	Dimensionless distance
V_f	Volume fraction of diffusing material
V_t	Constant in Figure 16.4 used to find local diffusion coefficients at V_f greater than 0.20
V_2	Diffusion coefficients at V_f equal 0.20 relative to diffusion coefficient at zero concentration (Figure 16.1 and Figure 16.4)
b	Thickness of cylindrical sample in Equation 16.24
c	Concentration of diffusing material
c_s	Surface concentration
c_0	Initial concentration
c_1	Concentration on exposed side of sample
c_2	Concentration on exit side of sample
c_∞	Concentration at equilibrium conditions
h	Surface mass transfer coefficient
h_{av}	Average surface mass transfer coefficient
k	Constant in Equation 16.6
k_2	Constant in Equation 16.20
l	Length of sample in Equation 16.23
t	Time
$t_{1/2}$	Time required to absorb (or desorb) one half of the equilibrium amount
w	Width of sample in Equation 16.23
x	Distance
Δp	Pressure difference of diffusing material across membrane
Φ_R	Local concentration is Figure 16.6

INTRODUCTION

Chapters 12 through 14 have dealt with chemical resistance, environmental stress cracking, and barrier polymers, respectively. Absorption and diffusion of the chemicals into polymers are important in each of these. Factors affecting absorption and diffusion in polymers are therefore of considerable importance and must frequently be included along with the Hansen solubility parameters (HSP) to make correlations and predictions for these phenomena. This chapter emphasizes the importance of surface resistance for absorption in polymers as this has been largely overlooked in the literature. The focus of much of the relevant literature has been on anomalous diffusion, but even in this context the influence of surface resistance has largely been neglected. Surface resistance can delay or prevent the absorption of solvents that should absorb readily based on simple HSP considerations. This could lead to a false sense of security based on short time testing only.

Absorption requires some degree of solubility. Therefore, equilibrium absorption can be expected to correlate with HSP. In studies of the absorption of a chemical into a polymer, its surface concentration is usually assumed to reach the equilibrium value immediately. As discussed in the

following, this is not always true. Whatever the rate at which the surface concentration increases, absorption will proceed according to the laws of diffusion, Fick's First Law, Equation 16.1, and Fick's Second Law, Equation 16.2. The latter is often called the diffusion equation. Its derivation can be found in Crank.[1] For the sake of simplicity, these equations are given here for diffusion in one dimension (x) only. For a constant diffusion coefficient,

$$F = - D_0(\partial c/\partial x) \tag{16.1}$$

$$\partial c/\partial t = \partial/\partial x \; (D_0 \partial c/\partial x) \tag{16.2}$$

The diffusion equation is derived in a very general way and also accounts for concentration dependent diffusion coefficients whenever this is encountered. F is the mass flux, D_0 is the (constant) diffusion coefficient or the diffusion coefficient at the lowest concentration if there is concentration dependence (see below), c is the local concentration, x is the distance in the x dimension, and t is the time. The solutions to the diffusion equation given in this chapter use the dry film thickness as reference. This is because it is far simpler to keep track of what is going on instead of continually adjusting local film thickness as a function of the amount of solvent present. When a diffusing solvent is present, for example, then the actual local thickness should be increased proportionately according to its local volume fraction.

The use of dimensionless variables to solve these equations makes the solutions more useful by making them applicable to all values of the combined variables. For this purpose the following are defined:

Dimensionless time:

$$T = D_0 t/L^2 \tag{16.3}$$

Dimensionless distance:

$$X = x/L \tag{16.4}$$

Dimensionless concentration:

$$C = (c - c_0)/(c_\infty - c_0) \tag{16.5}$$

L is the thickness of the plane sheet being considered. c_0 is the initial uniform concentration in the film. The (local) dimensionless concentrations rise from 0 to 1.0 in an absorption experiment where equilibrium absorption, c_∞, is finally obtained.

For the sake of completeness the predicted and experimentally confirmed exponential dependence of the diffusion coefficient on concentration, D(c), will be introduced at this early stage. A more detailed discussion of its significance is given in a special section below.

$$D(c) = D_0 e^{kc} = D_0 D_v \tag{16.6}$$

"k" is a constant that is valid up to a given concentration as discussed below. D_v is the increase in the diffusion coefficient over that at zero conditions for a given concentration. At the maximum concentration this becomes D_{max}, and for a constant diffusion coefficient it is 1.0.

Using these variables, Equation 16.2 can be rewritten in dimensionless form as Equation 16.7.

The dimensionless diffusion equation for an exponential diffusion coefficient is:

$$\partial C/\partial T = \partial/\partial X \; (D_v \partial C/\partial X) \tag{16.7}$$

The earliest edition of Crank's monumental work[1] has the advantage of many graphical solutions to the dimensionless diffusion equation being presented with plots that can be used with a high degree of accuracy. These plots include numerous reference lines not found in later editions.

STEADY STATE PERMEATION

In the absence of significant surface resistances, solving Equation 16.1 (or Equation 16.7) for steady state permeation in one direction only for a constant diffusion coefficient gives Equation 16.8.

$$F = -D_0(c_1 - c_2)L \tag{16.8}$$

The surface concentration on the exposed side, c_1, is usually assumed to be c_∞, and c_2 is usually assumed to be zero. Initially, c_1 will be less than c_∞ when there is a significant surface resistance on the exposed side, as discussed in the following. Likewise, c_2 will be greater than c_0 if there is a significant surface resistance on the low concentration side of the film. The preferred units for these quantities are F in $g/(cm^2 \times s)$, L in cm, c in g/cm^3, and D_0 in cm^2/s.

It can be seen from Equation 16.8 that the surface concentration on the exposed side determines the concentration gradient over the film, assuming c_2 is zero. This is a situation that seems to prevail in general, but exceptions are discussed below, and there will be significant surface resistance in presumably all cases as film thickness approaches zero. The surface concentrations, c_1 (or c_s), will be higher for closer matches in HSP between challenge chemicals and polymers. Therefore, it is not surprising that HSP correlations can be made when permeation rates for a large number of chemicals have been measured for a given polymer, as reported in Chapter 13. This is particularly true when the molecules involved are all relatively small. When the molecular sizes of the challenge chemicals become too large and/or their shape becomes sufficiently complicated with side groups and cyclic structures, simple HSP correlations are no longer possible. The diffusion coefficient is affected by these size and shape factors, and the HSP can no longer be used as a single correlating parameter. In addition, surface resistances can also become very significant, as discussed below and in Chapter 14. The molecular volume, V, of the challenge chemical has been used with some success to account for size effects, but this does not directly account for differences in shape. Examples of correlations for diffusion through chemical protective clothing, for example, demonstrated that molecular size had to be taken into account[2] (see also Figure 13.2 and the discussion in Chapter 13). The most reliable HSP correlations in these cases do not immediately consider the solvents with smaller molecules that may permeate faster than expected by comparison with all the others. Likewise, improved understanding and correlations are obtained by initially neglecting the solvents with larger molecules that do not permeate as fast as expected, in spite of close matches in HSP with those solvents that do permeate rapidly. Once a reliable HSP correlation is established without these obvious outliers, their behavior is better understood. Predictions then often become possible for other very small and/or very large molecular species as well.

THE DIFFUSION EQUATION

CONSTANT DIFFUSION COEFFICIENTS

Relevant solutions to Equation 16.2 or Equation 16.7 are used to measure diffusion coefficients. The diffusion equation must be solved with two boundary conditions and an initial condition. This discussion will consider a plane film exposed to absorbing chemical on two sides. The initial condition is chosen as a uniform concentration within a film, so that C is 0 for all X, regardless of whether the initial concentration is zero or not. Diffusion is also usually assumed to take place in one direction only, but side effects can become important in thicker samples as discussed below. The chemical concentration at the exposed surface(s) is assumed to immediately rise to the

equilibrium value. The second boundary condition is found at the middle of the free film exposed on two sides where there is no transfer in either direction. In other words Equation 16.1 is set equal to zero at this point.

For a constant diffusion coefficient, solving the diffusion equation with these conditions gives an initial straight-line absorption curve as a function of the square root of time. This is generally called Fickian diffusion. The straight line passes through the origin, and the time required to absorb one-half of the equilibrium amount, $t_{1/2}$, can be used in Equation 16.9 to find D_0.

$$D_0 = 0.049 \ L^2/t_{1/2} \qquad (16.9)$$

This equation is based on T having a value of 0.049 when half of the equilibrium amount has been absorbed. There is an identical result for desorption experiments where the time required for half of a uniformly absorbed material to leave the film also requires the same T value.

CONCENTRATION DEPENDENT DIFFUSION COEFFICIENTS

Solutions for the diffusion equation have also been generated for concentration dependent diffusion coefficients for the same boundary and initial conditions as described above. In this case it can be shown that Equation 16.7 reduces to Equation 16.10.[3–5]

$$\partial D_v/\partial T = D_v(\partial^2 D_v/\partial X^2) \qquad (16.10)$$

This equation has been solved numerically many times for different values of D_{max} for both absorption and desorption with a uniform initial concentration.[3–5] D_{max} is the ratio of the maximum diffusion coefficient found at the maximum concentration encountered in an experiment to D_0. The half-times calculated for both absorption and desorption were converted to F_a or F_d, respectively, their ratio to the value 0.049. These values are given in Table 16.1. F_a and F_d are the F_M for use in Equation 16.11. The correction factors for desorption experiments were also found for the time required for only one fourth of the material to leave the film in desorption experiments. This was necessary because of the extremely long experimental times (months) required for even this amount to leave, and also holds true for very thin films. These quarter-time correction factors for desorption were used to generate the results reported in Figure 16.1 and are discussed in the following.[6] The results reported in this figure confirm that F_a and F_d are correct and useful. The same diffusion coefficients were found by both absorption and quarter-time desorption measurements. The correction factors for the absorption measurements, F_a, were close to 2.0, whereas those for the quarter-time desorption measurements, F_d, were in the range of 40 to 144.

$$D(c) = F_M \times F_B \frac{0.049 \times L^2}{t_{\blacklozenge}} \qquad (16.11)$$

The factor F_B in Equation 16.11 is a related correction accounting for any surface resistance as discussed below. F_B will always be greater than 1 as a surface resistance slows the transport process and leads to an apparent diffusion coefficient that is too low.

The exponential increase in diffusion coefficient with concentration is expected based on free volume theory.[7] It is beyond the scope of this chapter to include this theory in detail. The main feature of diffusion in polymers is that the macromolecular chains are barriers to transport. Factors that either promote mobility of the chain segments or increase the distance between them will enhance the movement of smaller molecules. The transport occurs as very small movements rather than larger jumps. An increase in concentration of plasticizing smaller molecules leads to an increase in the free volume of the system, as the smaller molecules have more free volume associated with

TABLE 16.1
Correction Factors for the
Measurement of Concentration
Dependent Diffusion Coefficients
for Use in Equation 16.11

| D_{max} | Desorption | | Absorption |
	$(F_d)_{1/2}$	$(F_d)_{1/4}$	$(F_a)_{1/2}$
10^0	1.00	1.00	1.00
2	1.56	1.55	1.30
5	2.70	2.61	1.70
10^1	4.00	3.84	2.01
10^2	13.40	10.20	3.30
10^3	43.30	23.10	4.85
10^4	138.7	47.40	6.14
10^5	443	89.0	7.63
10^6	1,370	160.5	8.97
10^7	4,300	290	10.60
10^8	13,670	506	12.10

Note: $(F_d)_{1/2}$ is for desorption half-times, $(F_d)_{1/4}$ is for desorption quarter-times, and $(F_a)_{1/2}$ is for absorption half-times.

them than do polymers. Thus diffusion coefficients increase as solvent concentration increases. As can be seen in Figure 16.1 and Figure 13.1, the diffusion coefficient for common solvents increases by a factor of about 10 for an increase of solvent concentration 0.03 volume fraction at lower solvent concentrations. This corresponds to slightly more than doubling the diffusion coefficient for each added 0.01 volume fraction of solvent.

Concentration dependence in measuring diffusion coefficients by absorption can also be accounted for by the method of integrals given by Crank.[1] Treatment of the experimental data given by Crank with the correction factors given in Table 16.1 leads to exactly the same result for the exponential diffusion coefficients of chloroform in polystyrene as was found by the method of integrals. Both procedures require iterations as the true value of D_{max} is not known initially and must be estimated to find F_a (and a new D_{max}) until convergence is obtained.

SURFACE RESISTANCE

MATHEMATICAL BACKGROUND

The diffusion equation must be solved with the appropriate boundary conditions at the surfaces when significant surface resistances are encountered. For a film exposed on two sides, the absorption process then can be modeled with the following boundary condition at the surfaces:

$$F = h(c_\infty - c_s) \tag{16.12}$$

The surface mass transfer coefficient, h, has preferred units of cm/s. The surface concentration at any given time is c_s. One estimate of h can be obtained by plotting the weight gain against time. The limiting slope at time approaching zero is used to find F. As c_s is zero at time equal to zero, h can be estimated from this initial flux divided by c_∞.
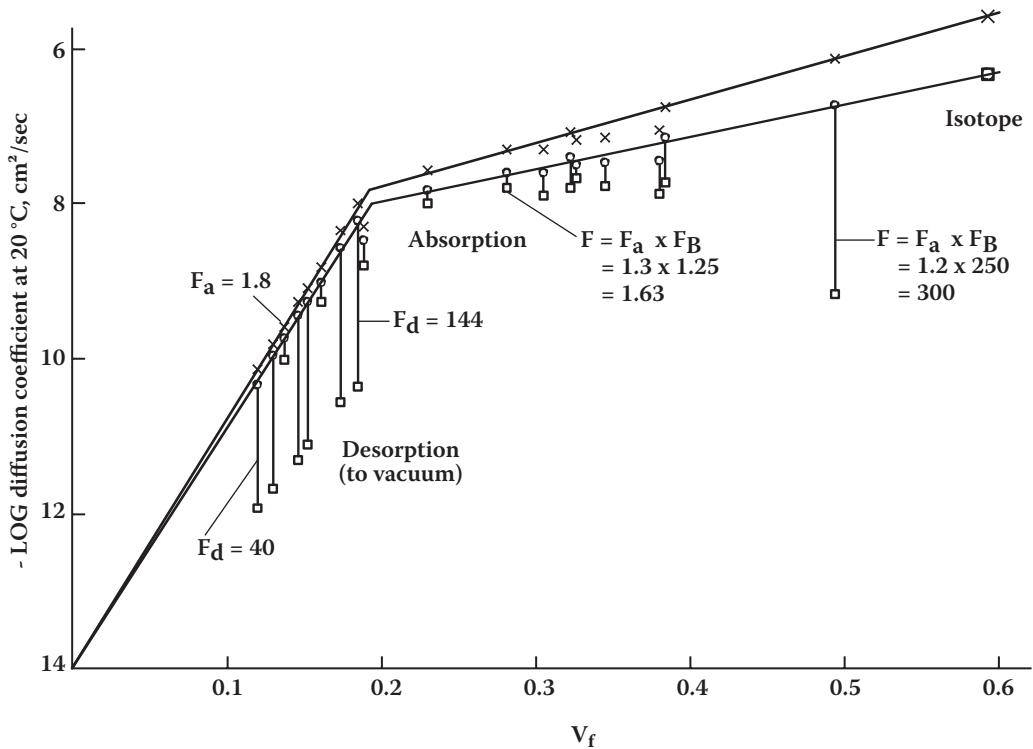
FIGURE 16.1 Diffusion coefficients for chlorobenzene in polyvinylacetate measured by absorption half-times, desorption quarter-times, and isotope experiments as a function of the volume fraction of chlorobenzene, V_f.[6] The lower curve is based on dry polymer content. The upper curve is based on total thickness. Corrections for surface resistance, F_B, are also required for V_f above about 0.2 volume fraction. In an extreme case for absorption with V_f near 0.5, the correction for surface resistance was a factor of 250.[21] (Reprinted from Hansen, C.M., *Prog. Org. Coat.*, 51(1), 55–66, 2004. With permission from Elsevier.)

It is useful to rewrite this boundary condition in dimensionless terms using the quantity B. This is the ratio of diffusion resistance, R_d, to that of surface resistance R_s. Thus,

$$B = R_d/R_s = (L/D_0)/(1/h) = hL/D_0 \qquad (16.13)$$

Large B is indicative of a diffusion-controlled process. For B = 1, $R_d = R_s$, and for lower B surface resistance dominates. Surface resistance becomes increasingly important as the film thickness decreases.

The dimensionless boundary condition corresponding to Equation 16.12 for use with Equation 16.7, considering the x direction only is

$$\partial C/\partial X = B(1 - C_s) \qquad (16.14)$$

For an exponential concentration dependence of the diffusion coefficient, this boundary condition can be used with Equation 16.10 as[3,5]

$$\partial D_v/\partial X = B \ln D_v \qquad (16.15)$$

TABLE 16.2
Correction Factors, F_B,
for Use with a Constant
Diffusion Coefficient in
Equation 16.11

B	1/B	F_B
∞	0	1.0
10	0.1	1.45
2	0.5	3.14
1	1	4.95
0.5	2	6.8
0.1	10	37.5

Note: This means that F_M is equal to 1.0 in this case.

SURFACE RESISTANCE IN ABSORPTION EXPERIMENTS

Solutions to the diffusion equation have been presented for various surface resistances (surface conditions) by Crank for a constant diffusion coefficient.[1] F_B has been evaluated from these graphical results as the ratio of the half-time for a given B value to 0.049. These results are reported in Table 16.2.

Equation 16.16 can be used for B less than about 0.5. At higher B values it is not exact.

$$F_B = (3.75/B) + 1 \tag{16.16}$$

As stated above, when surface resistance can be neglected, a plot of the (relative) uptake vs. the square root of time initially is a straight line that passes through the origin. When surface resistance becomes important, the delayed uptake can be seen as a form of time-lag phenomena, with a clear "S" shape. It is also interesting to note at this point that solutions to the diffusion equation with the boundary condition of an exponential increase of the surface concentration with time give absorption curves with exactly the same "S" shapes. Numerical solutions to the diffusion equation of the type described in Reference 3 and Reference 5 confirm that significant surface resistance leads to an exponential increase in the surface concentration. The factors leading to and controlling the prevailing surface concentrations are of major interest and not necessarily the fact that these increase in an exponential manner with time.

Figure 16.2 shows S-shaped curves for absorption in the COC polymer, Topas® 6013 from Ticona. Surface resistance is significant in all three cases shown, as can be seen by the S-shaped curves that do not pass through the origin.[8] The apparent B values for these cases are 10 for ethylene dichloride, 0.5 for diethyl ether, and 20 for propyl amine. Solvent absorption was followed in injection-molded samples for 13 solvents in cyclic olefinic copolymer (COC), 4 solvents in two different grades of polycarbonate (PC), and 2 solvents in the terpolymer acrylonitrile/butadiene/styrene (ABS). It was discovered that a surface resistance to absorption was significant in 19 of these 23 cases. Approximate surface mass transfer coefficients and approximate diffusion coefficients were determined where possible. There is no significant surface resistance to absorption in those cases where the absorbing molecules are smaller and linear such as for tetrahydrofurane, n-hexane, and 1,3-dioxolane in the COC polymer, and butyric acid in PC (Lexan® 104R, General Electric). When the challenge molecules are too large or bulky, no absorption occurs. Such systems included 1,4-dioxane, methyl isobutyl ketone, acetophenone, and phenyl acetate in the COC polymer. There
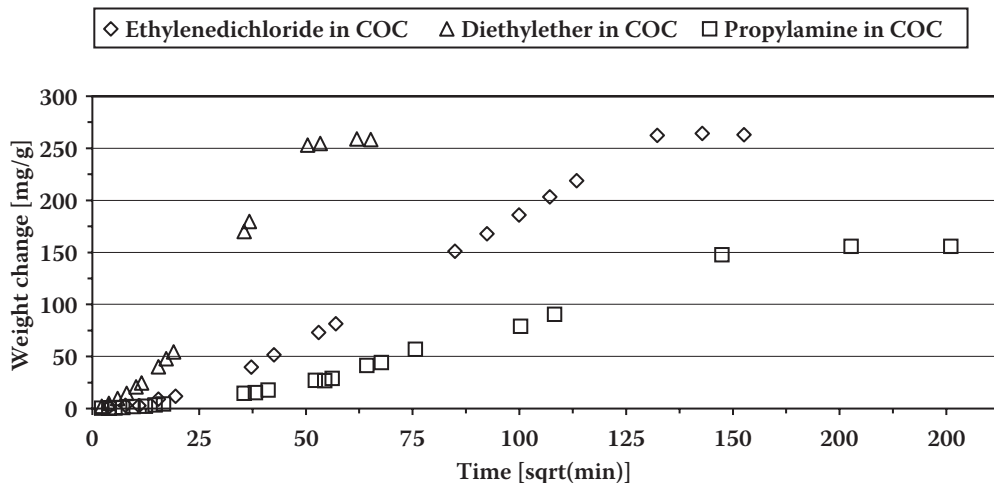
FIGURE 16.2 Absorption of ethylene dichloride, diethyl ether, and *n*-propylamine in a COC polymer, Topas® 6013, Ticona, at 23°C. (Reprinted with permission from Nielsen, T.B. and Hansen, C.M., *Ind. Eng. Chem. Research*, 44(11), 3959–3965, 2005. Copyright 2005 American Chemical Society.)

was no weighable absorption, even though HSP would predict this. The molecules can simply not get through the surface layer, and its resistance is therefore effectively infinitely large. Other examples of lack of absorption are oleic acid that simply does not absorb in the PC polymers or ABS. Between these extremes are situations where surface resistance clearly affects the absorption process. Surface resistance becomes significant when molecules can be transported away from the surface into the bulk of the polymer faster than they can be adsorbed/absorbed just at/in the surface.

SURFACE RESISTANCE IN PERMEATION EXPERIMENTS

As stated above, Equation 16.13 clearly shows that the importance of surface resistance will increase as film thickness decreases, and vice versa. This can be used in permeation measurements to find the true permeation coefficient as well as the sum of all other resistances to the transport process. One measures apparent permeation coefficients P_{app}, for different film thicknesses and extrapolates the inverse of the apparent transport coefficient versus the inverse of the film thickness to zero, corresponding to infinite film thickness. This is portrayed in Figure 16.3 for the permeation of water through an acrylic coating.[9] If a single measurement had been made at a film thickness of 40 microns, which is a normal film thickness, the apparent permeation coefficient would have been one-half that of the true permeation coefficient.

The data in this type of figure can be interpreted using the following set of equations:

$$F = \Delta p/(L/P_{app}) = \Delta p/(L/P_\infty + R_1 + R_2 + R_3 \ldots) \tag{16.17}$$

$$L/P_{app} = L/P_\infty + R_1 + R_2 + R_3 \ldots \tag{16.18}$$

$$1/P_{app} = 1/P_\infty + (R_1 + R_2 + R_3 \ldots)/L \tag{16.19}$$

The extrapolation to $1/L$ equal to zero gives the inverse of the true permeation coefficient, $1/P_\infty$, and the slope gives the sum of the resistances. Δp is the overall vapor pressure difference in the system, and the given R represent different sources of resistance.

Other extrapolations are possible to gain more information, depending on the situation.[10] One can find the vapor diffusion coefficient (resistance), for example, by varying the amount of liquid
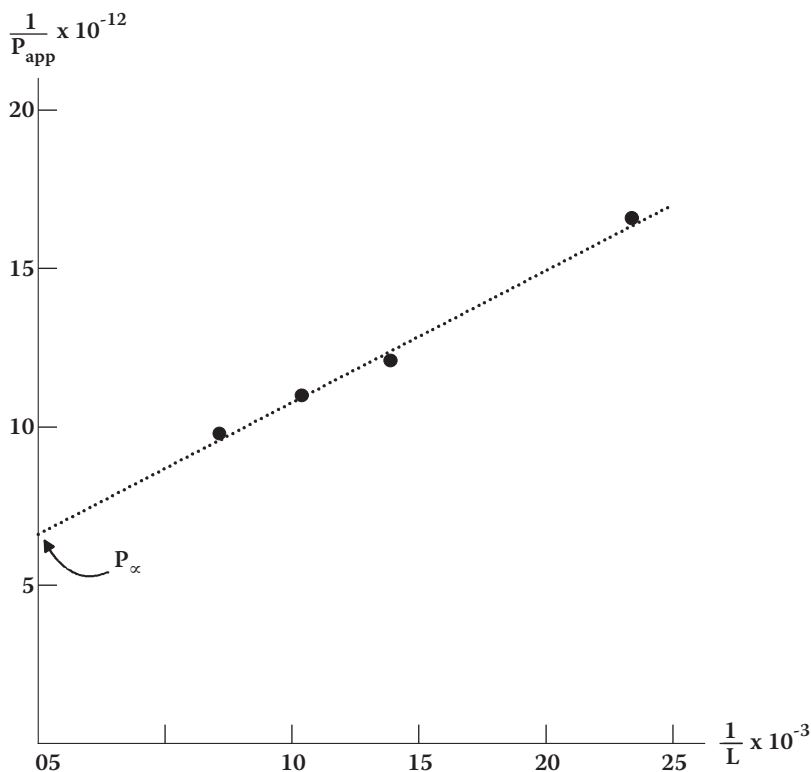
FIGURE 16.3 A plot of the inverse of the apparent permeability coefficient (P_{app} in kg Pa[1] s[1] m[1]) vs. the inverse of the film thickness (L in m) for an acrylic coating. Extrapolation to 1/L to zero gives the inverse of the true permeability coefficient. (Reprinted from Huldén, M. and Hansen, C.M., *Prog. Org. Coat.*, 13(3/4), 171–194, 1985. With permission from Elsevier.)

in a cup-type experiment. It has been found that these surface and vapor diffusion effects must be accounted for in cup-type and related experiments with thinner polymer films and porous types of materials. These include thinner paint films, wood in the fiber direction, and paper, for example.[9–11]

This type of experiment using paper as a film separated resistances for the permeation of the paper by water as well as for diffusion of water in air, (heat transfer) evaporation of the water, and an estimate of the surface resistances on the two sides of the paper.[10]

SURFACE RESISTANCE — A DISCUSSION

In the literature surface resistance has alternatively been called skin layer effect, surface condition, interfacial resistance, or boundary layer resistance, and leads to what is often called an induction time and "time-dependent" diffusion. In addition to the discussion and literature cited above, surface effects have been noted in many studies of diffusion in polymers. The following also deal with surface effects in the absorption of solvents into polymers.

A skin layer was found on the surface of injection molded polypropylene.[12] NMR microimaging was used to confirm that carbon tetrachloride absorption was retarded by this layer. The rapid surface cooling in the injection molding process gives a surface different from the interior, where the cooling rate (and orientation) is different. This effect is presumably found with many injection molded polymers.

McDonald et al. also arrived at the conclusion that surface flux limited diffusion of solvent into polymer could explain observed behavior such as Case II and transitions between Fickian

diffusion and Case II diffusion.[13] Toluene diffusion in polystyrene is discussed in detail. Case II diffusion involves a linear absorption curve when time is used rather than the customary square root of time. This is discussed in more detail below.

Shankar studied interfacial resistance in absorption experiments.[14] The conclusions were that non-Fickian characteristics can result from slow transfer to the surface layer, and that some of the observed features of anomalous sorption can be explained with the help of this model. Surface resistance was found to be particularly important in thinner sheets. Systematic variations in absorption phenomena with film thickness are a clear indication of a significant surface resistance. When there is a surface resistance, the surface concentration only slowly rises to the equilibrium value. Surface resistance in the methyl iodide-cellulose acetate system produced the characteristic S-shaped absorption curve.

Characteristic S-shaped absorption curves were found in the methylene chloride-PEEK system by Gryson et al.[15] The initial rate of absorption was found to be strongly dependent on the surface condition but the equilibrium values were not.

Surface resistance was shown to affect permeation through polymer films by Kim and Kammermeyer who measured actual concentration profiles in Nylon-6, cellulose acetate, and polyethylene membranes.[16] Water permeation through Nylon-6 films was studied for different film thickness. It was clearly shown that the surface concentration of water did not reach the equilibrium value at the equilibrium permeation rate unless the film thickness was greater than 0.05 cm at 35°C. Similar studies showed that there were also significant surface resistances for dioxane, benzene, and *n*-hexane in polyethylene, and for water in cellulose acetate.

Hwang and Kammermeyer showed significant surface resistance by studying permeation as a function of film thickness for water in acetyl cellulose acetate and Nylon-6, hydrogen through stainless steel, and *p*-dioxane through Nylon-6 and polyethylene.[17]

Skaarup[18] performed many permeation experiments on Polyamide 6 (PA 6) (BASF Ultramid B4) and polyvinylacetate (Hoechst, Mowilith 50) where surface resistance was significant. Of particular interest are the studies on PA 6 where the permeation of ethyl laurate, 2,4-dimethyl-2-pentanol, benzyl alcohol, *n*-butanol, ethyl acetate, and *n*-pentane was studied. Skaarup arrived at the following general relation for the permeation of these liquids through PA

$$h_{av} = k_2(D_{av}/A^{1/2}) \qquad (16.20)$$

h_{av} (in cm/s) is the average surface mass transfer coefficient, D_{av} (in cm²/s) is the average diffusion coefficient in the film (see Equation 16.21), and A (in cm²) is the (minimum) cross-sectional area of the molecule in question. k_2 is a constant with the value approximately $4.5(10)^{-6}$. This equation indicates that a molecule in the surface of a polymer will proceed inward in direct proportion to the diffusion coefficient. It likewise indicates that the greater the cross-sectional area of the molecule, the more difficulty it will have to reside at the surface in a condition where it can take a small jump into the bulk. h on the exposed side of the films was approximately 1/3 of that on the exit side. The reason for this is thought to be that the orientation of molecules leaving the film is directed more toward the exit surface, whereas the orientation of molecules approaching the entry side is more random. A molecule landing "sideways" and hitting a polymer segment will be rejected. The right orientation at the right place allows adsorption/absorption. The significance of the surface resistances can be demonstrated by the film thickness at which the resistance from diffusion within the film is equal to the sum of the two surface resistances. This was about 180 microns or higher for the linear aliphatic molecules, and increased for more complicated structures.

D_{av} can be found from Equation 16.21 as the logarithmic mean where D_1 is the diffusion coefficient on the exposed side and D_2 is the diffusion coefficient on the exit side.

$$D_{av} = (D_1/D_2 - 1)/\ln(D_1/D_2) \qquad (16.21)$$

This equation shows how much the average diffusion coefficient differs from that at essentially zero concentration corresponding to D_2. If the ratio D_1/D_2 is 10 then D_{av} is 3.9 times larger than D_1. This implies that concentration dependent diffusion can lead to significant errors when diffusion and permeation coefficients at very low concentrations are needed. D_1/D_2 equal to 10 implies that the concentration difference is only about 0.03 volume fraction across the membrane when rigid polymers are involved. For elastomers this same ratio implies a concentration difference near 0.15 volume fraction, as judged from the diffusion coefficient data reported in Figure 16.1 at concentrations above about 0.20 volume fraction where the system is above its glass transition temperature. These same considerations are valid for permeation coefficients since:

$$P = DS \tag{16.22}$$

P is the permeation coefficient measured at the given steady state concentration difference, $(c_1 - c_2)$, and S is the solubility coefficient. If D_1 is 10 times greater than D_2 then P is approximately 3.9 times larger than would have been measured for an extremely low concentration difference across the membrane.

SIDE EFFECTS

Corrections for absorption or desorption from the sides of thicker samples should be applied to measured diffusion coefficients if there is significant diffusion through the sides of thicker samples. Equation 16.23 for diffusion in plane samples of isotropic media can be used for this purpose.[19]

$$D_0 = D_{app}/(1 + L/l + L/w)^2 \tag{16.23}$$

D_{app} is the apparent diffusion coefficient found from initial slope measurements[1] or Equation 16.9 if there is a linear absorption curve as far as $t_{1/2}$ when the square root of time is used. The length and width of the film are l and w, respectively, with L being retained as the thickness. It can be seen that D_0 and D_{app} are equal to the extent that the second and third terms in Equation 16.18 are not significant. Conventional tensile bars, for example, have significant side effects when they are used to measure diffusion coefficients. The uptake is more rapid than otherwise anticipated, so the apparent diffusion coefficients must be reduced accordingly. Tensile bars that are 4 mm thick and 10 mm wide will require corrections that are at least as great as a factor of 1.96. A square sample that is 10 mm on each side and 1 mm thick requires a correction for end effects equal to 1.44.

For cylindrical geometry a derivation similar to that used to find Equation 16.23 results in Equation 16.24.

$$D_0 = D_{app}/(1 + b/R)^2 \tag{16.24}$$

R is the radius of the cylinder and b is its thickness. These equations are based on the initial uptake (or loss) to evaluate D_{app}. Here again, an easy procedure is to extrapolate the initial slope on a plot of uptake versus the square root of time to a fictive $t_{1/2}$ found when the relative uptake is equal to 0.5. This value for $t_{1/2}$ can be used in Equation 16.9 to find D_{app}.

MEASURING DIFFUSION COEFFICIENTS WITH SURFACE RESISTANCE AND CONCENTRATION DEPENDENCE

It was necessary to measure diffusion coefficients over as wide a range as possible in order to solve the diffusion equation to simulate film formation by solvent evaporation.[3,20] This was done by comparison of experimental results with solutions to the diffusion equation accounting for both

concentration dependence and surface resistance at the same time. These techniques are reported elsewhere.[3–5,21] The technique used was to interpret the experiments initially assuming that the diffusion coefficient was a constant at the concentration assigned to the experiment. Corrections to this estimate (multiplying factors) were then made by comparison with suitable solutions to the diffusion equation using the data in Table 16.1 in Equation 16.11. The correction factors, F_a, at low concentrations were close to 1.5–2.0 (corresponding to increases of from 50 to 100%) for the usual step-wise absorption experiments from one concentration to a slightly higher one. The correction factors, F_d, were well above 100 for desorption measurements from an equilibrium state near 15–20%vol solvent to vacuum. The results in Figure 16.1 show that the same diffusion coefficients were found in both cases. Absorption experiments only were relevant above about 20%vol because there is a marked change in diffusion behavior at concentrations above and below this value (for the system chlorobenzene and polyvinylacetate). When concentrations reach higher than about 20%vol, the correction factors for surface resistance, F_B, increase rapidly. They can become as high as 100 or more.[21] The total diffusion coefficient curve from 0 to 100% solvent (chlorobenzene) was completed with a self-diffusion coefficient and several isotope experiments.[3] The isotope experiments are for very high solvent concentrations that correspond to liquid lacquer formulations. The solvent-in-polymer diffusion coefficient for chlorobenzene in polyvinylacetate increases more than 9 decades as the solvent concentration increases from essentially zero to 100%, where the self-diffusion coefficient is $1.65(10)^5$ cm^2/s.

These coordinated absorption and desorption experiments were necessary to determine the true diffusion coefficients at all concentrations so that the solutions to the diffusion equation for film drying by solvent evaporation were correct.[3,20] It is also necessary to consider concentration dependence simultaneously with surface resistance in many cases of practical importance. Surface resistance has been present in many studies reported in the literature and clearly affects many results involving diffusion in polymers, but only rarely has there been mention of this fact. This situation naturally led to solving the diffusion equation with relevant values for diffusion coefficients and surface resistances for additional situations of interest. The overall result was a simple explanation for the various types of so-called anomalous diffusion. It is the balance between the (concentration-dependent) diffusion resistance and the surface resistance that determines whether the diffusion is "Fickian" or whether it is presumed to be anomalous. This is discussed in the next sections.

FILM FORMATION BY SOLVENT EVAPORATION

The process of film formation by solvent evaporation has been fully described using the diffusion equation with a significant surface resistance and local diffusion coefficients found from the data in Figure 16.1. Loss of solvent was followed experimentally for about 2 years from an initial V_f of 0.75 until it was totally lost.[3,20] Surface resistance was significant at concentrations above about 0.2 volume fraction solvent in the system that was studied most extensively (chlorobenzene in polyvinylacetate). This was also confirmed by the calculations since the surface concentration fell to essentially zero when this amount was reached, and the continued loss of solvent was controlled by internal diffusion to the surface. In this situation h is affected by factors such as vapor pressure and latent heat of the solvent, heat transfer to the surface, and air velocity past the surface. The local diffusion coefficient changed from $5(10)^{-7}$ cm^2/s initially to $1(10)^{-14}$ cm^2/s at zero concentration. The experimental and calculated curves are reported in Figure 16.4.

The process of solvent loss takes place in two distinct stages. Surface resistance controls the first stage, whereas the second stage is controlled by the rate at which solvent molecules can diffuse to the film/air surface in order to evaporate.

The quantity V_2 in Figure 16.4 is given as 10^6. As can be seen in Figure 16.1, where diffusion coefficients are reported for the same system, this is the extent of the variation of the diffusion coefficient from 0 concentration up to C_A, the concentration at the break in the curve. V_t is a fictitious diffusion coefficient to calculate the diffusion coefficients at concentrations above C_A.
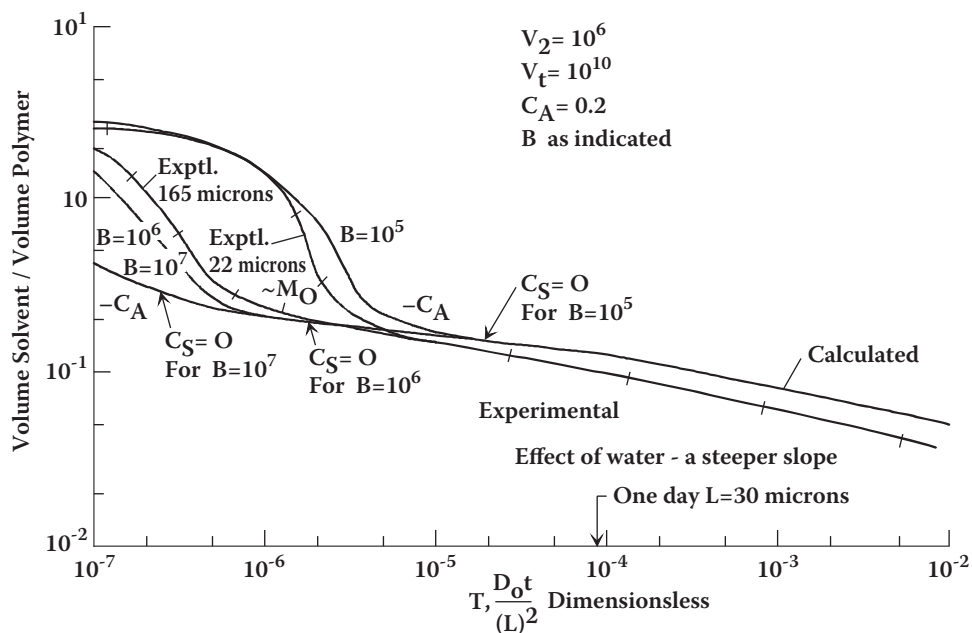
FIGURE 16.4 Calculated and experimental drying curves for the evaporation of chlorobenzene from polyvinyl acetate.[3,20] See the discussion in the accompanying text.

Diffusion coefficients were calculated for each local site in the films. The iterative procedure at each successive time interval was that described in Crank[1] as the Crank–Nicolson method. The films were divided into a sufficient number of finite difference elements to assure correct results.

Film drying in a climatized room was faster than film drying in a vacuum apparatus, where diffusion coefficients were measured. Absorbed water plasticizes the film. The calculated and measured desorption curves under vacuum coincided at long times (several months). Vacuum does not hasten release of solvent by diffusion at longer times. It only makes certain that the surface concentration is zero, which it will be in almost all cases anyway.

ANOMALOUS DIFFUSION (CASE II, SUPER CASE II)

For absorption with a constant diffusion coefficient one normally finds that the initial weight gain is linear with the square root of time as stated above. This is called Fickian or normal diffusion. In Case II diffusion, the weight increases linearly with time. This is largely a result of concentration dependent diffusion coefficients with a large jump in concentration. This is true even when there is very little surface resistance of significance.[5] Super Case II emerges as the surface resistance becomes more significant relative to the diffusion resistance.[5] Uptake is linear with time early in the process, but at some longer time the rate of gain increases markedly. See Figure 16.5. This change occurs when the diffusing material reaches the middle of a sheet exposed on both sides, for example. This can be seen in Figure 16.6 where concentration gradients have been calculated for Super Case II behavior. Simultaneous diffusion and surface resistance combine in a special way to produce this behavior. The chronology of the events is that surface concentration increases as time goes on. There is an advancing front into the film that is somewhat more pronounced than that shown in Figure 16.6, because the distances in this figure are based on dry film thickness. When the concentration at the center of the film starts to increase above zero, the rate of absorption also begins to increase. The concentration profiles ultimately become flat at moderate elapsed time, as diffusion within the film is now rapid compared to the surface resistance. The diffusion resistance
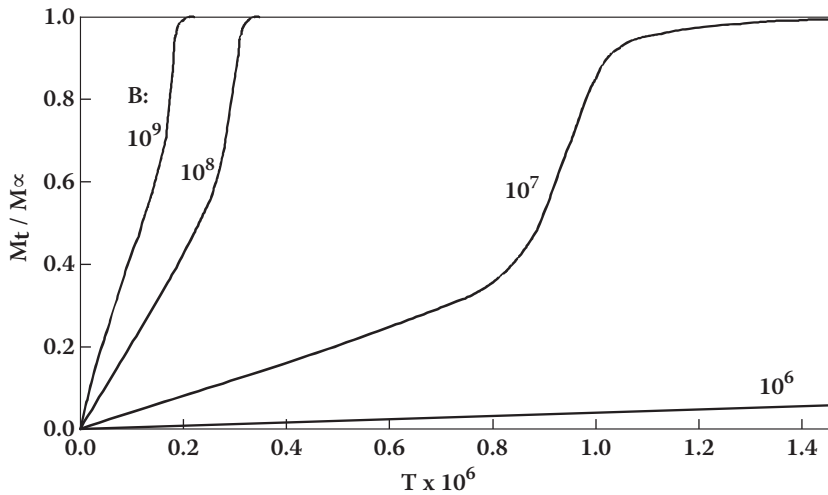
FIGURE 16.5 Solvent uptake curves for various values of B and concentration dependent diffusion coefficients equal to those reported for chlorobenzene in polyvinylacetate (See Figure 16.1). B is the ratio of diffusion resistance to surface resistance, including concentration dependence. (Reproduced from Hansen, C.M., Diffusion in Polymers, *Polym. Eng. Sci.*, 20(4), 252–258, 1980. With permission from the American Chemical Society.)
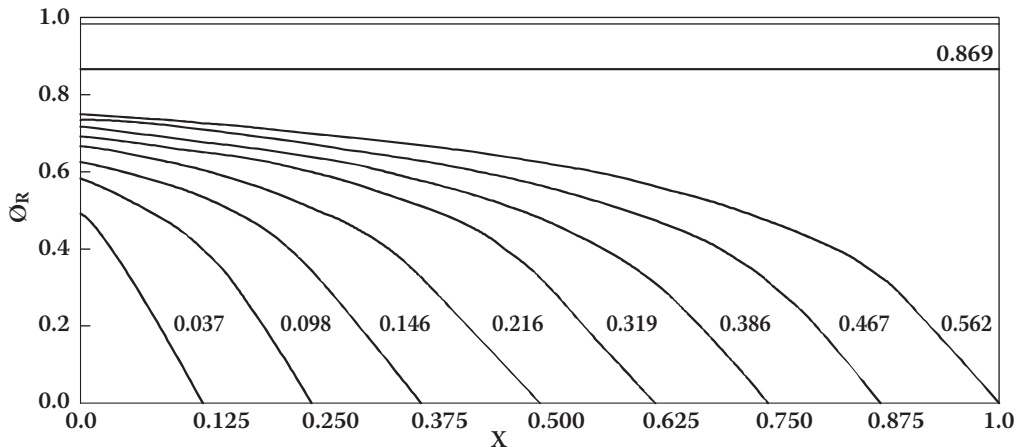

FIGURE 16.6 Concentration gradients for conditions corresponding to Super Case II type (anomalous) diffusion. Values on the curves are relative weight gains. $\varnothing_R$ is the local concentration. (Reproduced from Hansen, C.M., *Polym. Eng. Sci.*, 20(4), 252–258, 1980. With permission from the American Chemical Society.)

becomes less and less as the concentration in the middle of the film increases, and the rate of uptake increases. There is still another effect at very long times where the surface resistance begins to be more important again relative to the diffusion resistance. The rate of weight gain decreases just before the equilibrium value is attained.

The concentration gradients in Figure 16.6 are for the curve in Figure 16.5 for B = 10⁷. This is a typical Super Case II type curve with initial absorption linear with time followed by a sudden increase in the absorption rate as the solvent reaches the center of a film exposed on two sides. The final leveling off at very long times is also characteristic of Super Case II. The absolute value of B depends on the degree of concentration dependence over the selected concentration interval

in the given case. See Reference 5 for greater detail. The parameters chosen to calculate this curve are realistic.

GENERAL COMMENTS

Discussion of the various other explanations for anomalous diffusion is beyond the scope of this chapter. These discussions are focused on time-dependent replication of the observed diffusion phenomena, such as an advancing front,[22] and on explanations based on stress relaxation phenomena at the head of this advancing front.[23,24] Whereas these may have aspects of validity, they can only be convincing when the verifiable surface resistances and the verifiable exponential concentration dependence of the diffusion coefficient are also taken into account. It would appear that enhanced stress relaxation, like the increase of diffusion coefficient with solvent concentration, is dependent on the increase in free volume brought locally by the solvent molecules themselves. The measurement of surface resistances and concentration-dependent diffusion coefficients did not require use of any mathematical tools or explanations other than the diffusion equation solved with appropriate initial and boundary conditions. There were advancing fronts involved both in the mathematics and in the samples in the experiments. The simple approach of solving the diffusion equation with a verifiable (exponential) concentration-dependent diffusion coefficient, along with appropriate and verifiable parameters for the boundary conditions, explains and replicates both the absorption and the desorption of solvents in polymers over an extremely large concentration range. This is true with and without significant surface resistance.

The methodology and concepts presented in this chapter on diffusion in polymers combined with the methodology and concepts in the rest of this handbook should provide insight into many situations of industrial and theoretical interest. These include controlled release of drugs, absorption and transport through polymeric packaging of various kinds, improved prediction of the behavior of chemical protective clothing, absorption into coatings, release of absorbed chemicals from plastics, release of sterilization gas, etc.

CONCLUSION

Many organic liquids are aggressive with respect to many types of polymers. Predicting aggressive behavior is important, and the absorption of the organic liquids into the polymers is a key factor in this respect. This absorption can be strongly affected by both surface phenomena and the rate of diffusion within the bulk of the polymer. This chapter has emphasized the importance of surface resistance in this process. Additional material on diffusion in polymers including simple mathematical descriptions of film drying by solvent evaporation and so-called anomalous diffusion have been included to present several aspects of the importance of surface resistance to contribute to its better understanding.

There is no surface resistance to absorption where the absorbing molecules are small enough and/or linear. When the challenge molecules are too large or bulky, no absorption occurs, even though Hansen solubility parameter considerations lead one to predict that this is clearly expected. The molecules can simply not get through the surface layer, and its resistance is therefore effectively infinitely large. Between these extremes are situations where surface resistance necessarily affects the absorption process. Surface resistance becomes significant when molecules can be transported away from the surface into the bulk of the polymer faster than they can be adsorbed/absorbed just at/in the surface.

The simple approach of solving the diffusion equation with appropriate and verifiable parameters for the boundary conditions explains and replicates both the absorption and desorption of solvents in polymers over an extremely large concentration range. It is not yet possible to predict

which systems will give significant surface resistance to absorption. Experimental studies are still required, but some similarity in HSP must be present for absorption to occur in any event.

REFERENCES

1. Crank, J., *The Mathematics of Diffusion*, Oxford University Press, Oxford, 1956.
2. Hansen, C.M. and Hansen, K.M., Solubility parameter prediction of the barrier properties of chemical protective clothing, *Performance of Protective Clothing: Second Symposium, ASTM STP 989*, Mansdorf, S.Z., Sager, R., and Nielsen, A.P., Eds., American Society for Testing and Materials, Philadelphia, PA, 1988, pp. 197–208.
3. Hansen, C.M., *The Three Dimensional Solubility Parameter and Solvent Diffusion Coefficient, Their Importance in Surface Coating Formulation,* Doctoral dissertation, Danish Technical Press, Copenhagen, 1967.
4. Hansen, C.M., The measurement of concentration-dependent diffusion coefficients — the exponential case, *Ind. Eng. Chem. Fundam.*, 6(4), 609–614, 1967.
5. Hansen, C.M., Diffusion in polymers, *Polym. Eng. Sci.*, 20(4), 252–258, 1980.
6. Hansen, C.M., Aspects of solubility, surfaces, and diffusion in polymers, *Prog. Org. Coat.,* 51(1), 55–66, 2004.
7. Korsmeyer, R.W., Von Meerwall, E., and Peppas, N.A., Solute and penetrant diffusion in swellable polymers. II. Verification of theoretical models, *J. Polym. Sci.: Polym. Phys. Ed.,* 24, 409–434, 1986.
8. Nielsen, T.B. and Hansen, C.M., Significance of surface resistance in absorption by polymers, *Ind. Eng. Chem. Res.*, 44(11), 3959–3965, 2005.
9. Huldén, M. and Hansen, C.M., Water permeation in coatings, *Prog. Org. Coat.*, 13(3/4), 171–194, 1985.
10. Nilsson, E. and Hansen, C.M., Evaporation and vapor diffusion resistance in permeation measurements by the cup method, *J. Coat. Technol.*, 53(680), 61–64, 1981.
11. Hansen, C.M., Potential errors in water/water vapor permeation measurements using the cup method, *Färg och Lack*, 39(3), 57–60, 1993.
12. Abbott, R.J., Chudek, J.A., Hunter, G., and Squires, L., Skin layer effects on the diffusion of carbon tetrachloride into injection moulded polypropylene studied by ^{1}H NMR microimaging, *J. Mater. Sci. Lett.*, 15, 1108–1110, 1996.
13. McDonald, P.J., Godward, J., Sackin, R., and Sear, R.P., Surface flux limited diffusion of solvent into polymer, *Macromolecules*, 34, 1048–1057, 2001.
14. Shankar, V., Influence of interfacial resistance on kinetics of sorption, *Polymer*, 22, 748–752, 1981.
15. Grayson, M.A., Pao, P.S., and Wolf, C.J., Transport of methylene chloride in poly(aryl-ether-ether-ketone) (PEEK), *J. Polym. Sci.: Part B: Polym. Phys.*, 25, 935–945, 1987.
16. Kim, N.K. and Kammermeyer, K., Actual concentration profiles in membrane permeation, *Sep. Sci.*, 5(6), 679–697, 1970.
17. Hwang, S.T. and Kammermeyer, K., Effect of thickness on permeability, in *Permeability of Plastic Films and Coatings*, Hopfenberg, H.B. Ed., Plenum, New York, 1974, pp. 197–205.
18. Skaarup, K., Abstract, Lecture at Nordic Polymer Days, 1988; *Grænseflademodstand ved Diffusionsprocesser I Polymerer,* Danmarks Ingeniør Akadami, Kemiafdelingen (in Danish) 1981, Surface Resistance in Diffusion Processes in Polymers (in English).
19. Marom, G., The role of water transport in composite materials, in *Polymer Permeability*, Comyn, J., Ed., Elsevier, London, 1985, chap. 9.
20. Hansen, C.M., A mathematical description of film drying by solvent evaporation, *J. Oil Colour Chem. Assn.*, 51(1), 27–43, 1968.
21. Hansen, C.M., Diffusion coefficient measurements by solvent absorption in concentrated polymer solutions, *J. Appl. Polym. Sci.*, 26, 3311–3315, 1981.
22. Windle, A.H., Case II sorption, in *Polymer Permeability*, Comyn, J., Ed., Elsevier, London, 1985, chap. 3.
23. Petropoulos, J.H., Interpretation of anomalous sorption kinetics in polymer-penetrant systems in terms of a time-dependent solubility coefficient, *J. Poly. Sci. Polym. Phys. Ed.*, 22, 1885–1900, 1984.

24. Sanopoulou, M., and Petropolous, J.H., Systematic analysis and model interpretation of micromolecular non-fickian sorption kinetics in polymer films, *Macromolecules*, 34, 1400–1410, 2001.