
13 Applications — Barrier Polymers

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ABSTRACT

The permeation coefficient, **P**, of a liquid or a gas through a polymer is given by the product of the diffusion coefficient, **D**, and the solubility coefficient, **S**: $\mathbf{P} = \mathbf{DS}$. **S** correlates with the Hansen solubility parameters (HSP). At low permeant concentrations **D** is a constant. However, as the permeant concentration increases, its plasticizing effect on the polymer becomes significant, and the diffusion coefficient increases markedly. This effect can be very significant. The successful correlations of permeation phenomena with HSP are thought to be largely a result of this exceptional dependence of **D** on the dissolved permeant. As the amount of permeant being dissolved increases with closer matches of the HSP for permeant and barrier polymer, the end result is that both **S** and **D**, and therefore **P**, are functions of the HSP match. HSP correlations are given for breakthrough times in chemical protective clothing, permeation rates through barrier polymers, and barrier polymer swelling. Both liquids and gases are treated. Absorption and diffusion in polymers is treated extensively in Chapter 16.

INTRODUCTION

The permeation of a liquid or a gas through a polymer can be described by the relation

$$\mathbf{P} = \mathbf{DS} \quad (13.1)$$

P, the permeation coefficient, is the product of the diffusion coefficient, **D**, and the solubility coefficient, **S**. The diffusion coefficient indicates how fast the permeant molecules can move through the polymer. The solubility coefficient indicates how much of the permeant can be dissolved in the polymer. The amount dissolved in the polymer determines the concentration gradient over a film, and the concentration gradient is the driving force for mass transport. When solubility is higher, the concentration gradient is correspondingly higher, and, assuming the same diffusion coefficient, mass transport will be proportionately higher. **S** will be lower when the HSP of the barrier film and a solvent are very different.

A significant factor affecting **D** is the molecular size and shape of the permeant molecules. Larger molecular size and more complex and bulky molecular shape are major factors that lead to lower diffusion coefficients. The diffusion coefficient for oxygen in polyvinyl chloride (PVC) is well over a million times greater than that of *n*-hexane (at low concentrations) in the same polymer.¹ This difference in diffusion coefficients is a result of differences in molecular size. Likewise, it has been found that the rate of diffusion at the same concentration is about the same for different solvents with approximately the same size and shape, even though they may have different solubility parameters (but not so different that both are able to dissolve in the polymer at the level of comparison).²⁻⁴ The polymers in these studies were a copolymer of 87% vinyl chloride and 13% vinyl acetate, polyvinyl acetate, and polymethyl methacrylate.

CONCENTRATION-DEPENDENT DIFFUSION

Low molecular weight liquids are plasticizers for polymers if they can be dissolved in them. Water, for example, can significantly soften many polymers even though it is dissolved to only a few percent. The low molecular weight materials can greatly reduce the glass transition temperature of their mixtures with a polymer as they have considerably more free volume associated with them than the polymers themselves. This extra free volume allows easier polymer segmental motion. The diffusion of the smaller species (and other species) becomes faster as their local concentration and plasticizing effect become greater.

The solvent diffusion coefficient data in Figure 13.1 were first presented in Reference 3. See also Chapter 16. This figure shows diffusion coefficients for several solvents in polyvinyl acetate (PVAc) at 25°C. The diffusion coefficient for water shown in the figure was found by absorption and desorption experiments in thin films where a correction for the surface resistance was also required.⁵ See Chapter 16. It can be seen in this figure that for moderate solvent concentrations in this rigid polymer, the local diffusion coefficient increases by a factor of about 10 for an increase in solvent concentration of about 3 to 4 vol%. As this behavior is general for solvents in polymers, a rule of thumb indicates that the local diffusion coefficient for solvents in rigid polymers can increase by a factor of about one million when about 20 vol% solvent is present compared with the solvent-free state.³⁻⁷ This rule of thumb assumes that the polymer behaves as a rigid polymer over the concentration range being considered. This difference corresponds to the speed of a snail in the woods compared with a modern jet airliner.

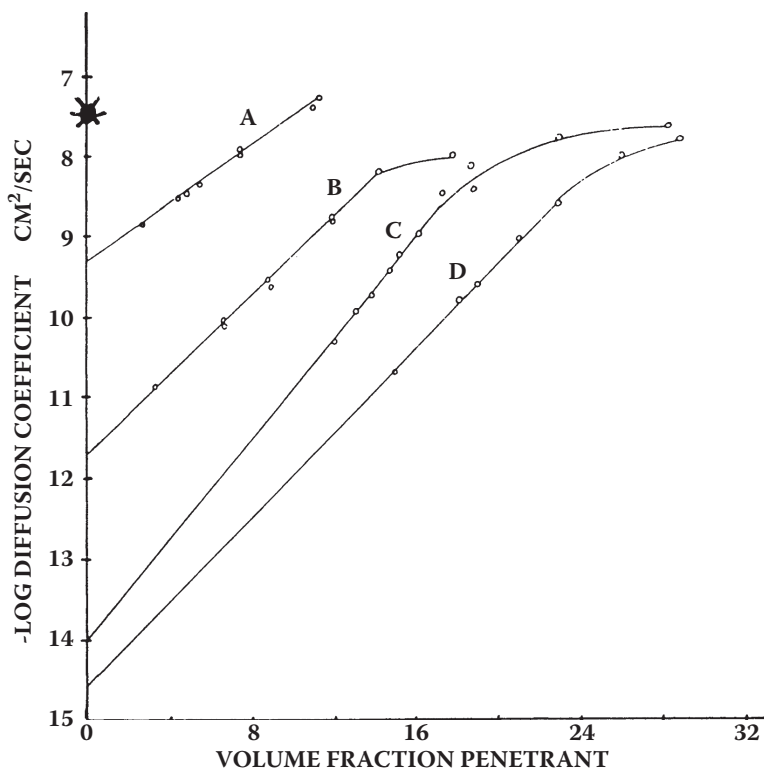


FIGURE 13.1 Diffusion coefficients in polyvinyl acetate at 25°C for methanol (A), ethylene glycol monomethyl ether (B), chlorobenzene (C), and cyclohexanone (D). Original data are in Reference 3. The data point for water (*) is included for comparison. (From Hansen, C.M., *Permeability of polymers, Pharmaceutical and Medical Packaging* 98, 1998, 7.12 With permission.)

Concentration-dependent diffusion coefficients are also found for elastomers. Here, the rule of thumb is that the diffusion coefficient increases by a factor of about 10 for an increase in solvent concentration of about 15 vol%.⁷ This shows that liquid contact with chemical protective clothing, for example, leads to concentration-dependent diffusion coefficients because the amount taken up at the contact surface on liquid contact is very often more than 15%.

Concentration-dependent diffusion has been discussed at length by Crank.⁸ It is also discussed here because it is a major factor in the success of HSP correlations of permeation phenomena. The Crank-Nicholsen finite difference treatment for concentration-dependent diffusion⁸ was extended by Hansen³ and used to describe film formation by solvent evaporation,⁴ to explore what is termed anomalous diffusion,⁵ to develop an easy method to evaluate data leading to concentration-dependent diffusion coefficients,⁶ and to account for the effects of concentration-dependent diffusion and surface boundary resistance simultaneously.⁵⁻⁷ Klopfer⁹ developed analytical solutions involving concentration-dependent diffusion for many situations found in practical building applications, particularly with respect to transport of water in building materials. Concentration-dependent diffusion can be handled properly without great difficulty for most situations of practical interest. Neglect of this effect can lead to errors, the significance of which will increase with increasing amounts of the dissolved materials.

In addition to demonstrating concentration dependence, the diffusion coefficient data for PVAc in Figure 13.1 also show the well-established relations that those solvents with larger and more complicated chemical structures are those with lower diffusion coefficients. Water has one “significant” atom, methanol has two, and ethylene glycol monomethyl ether (EGMME) has five. The diffusion coefficient for water in PVAc at low concentration, D_0 , is 10,000 times larger than that for the latter. An example of how to estimate diffusion coefficients in PVAc for other liquids, such as methylene chloride, is as follows. The diffusion coefficients in PVAc for methylene chloride, with three significant atoms, can be expected to be somewhat lower than those for methanol, but much higher than those for EGMME. Planar chlorobenzene diffuses more rapidly than nonplanar cyclohexanone, even though the number of significant atoms is the same. Another type of comparison which is possible is to state that the diffusion coefficients for toluene are expected to be close to those for chlorobenzene because of a similarity in molecular size and shape. This was confirmed by solvent retention studies where toluene and chlorobenzene were retained in identical amounts in a film of VYHH® (87 wt% vinyl chloride, 13 wt% vinyl acetate, Union Carbide). Toluene, which does not dissolve this polymer, was introduced by placing a completely dry polymer film in a closed container over toluene vapors.

Diffusion can be expected to be slower in more rigid polymers, i.e., those with higher glass transition temperatures, unless the rigidity is such as to allow decided holes of suitable size to enable quite rapid diffusion of much smaller molecules. These considerations lead to the best combination of properties for a barrier polymer as being one with a high glass transition temperature and with HSP far removed from those of the permeant. If, in practice, this leads to water sensitivity, an alternate strategy, such as a laminated system, may be required.

SOLUBILITY PARAMETER CORRELATIONS BASED ON PERMEATION PHENOMENA

SOLUBILITY PARAMETER CORRELATIONS OF BREAKTHROUGH TIMES

Extensive permeation studies and collections of permeation data are available within the chemical protective clothing industry.^{10,11} Such data can also be used to establish correlations with HSP. A list of HSP for barrier polymers used in chemical protective clothing has been published¹² based on data by Forsberg and Olsson.¹⁰ Some of these correlations have been improved in most instances by correlating the more extensive data of Forsberg and Keith.¹¹ The definition of a “good” solvent which was used for these correlations was that the breakthrough time was less than some selected

TABLE 13.1
HSP Correlations of Breakthrough Times for Barrier
Polymers Typically Used in Chemical Protective Clothing.
Units are MPa^{1/2}

Type	δ_D	δ_P	δ_H	Ro	V Limits	FIT	No.
Neoprene®	16.0	8.8	4.0	10.1	None	0.574	66
Neoprene	19.0	8.0	0.0	13.2	71.0/172	1.000	50
Butyl	17.0	1.5	0.0	7.3	71.0/175.8	0.902	86
Viton®	15.6	9.6	7.8	7.1	72.6/148.9	0.896	77
Nitrile	19.8	13.3	2.2	13.6	84.3/177.2	0.907	58
Challenge 5100®	16.6	7.0	3.8	2.3	None	0.925	116
PE	16.5	2.7	6.1	7.9	None	0.969	32

Note: "Good" solvents in these correlations have breakthrough times of less than 1 h.

value, either 20 min, 1 h, or 4 h. Table 13.1 includes some of these improved HSP correlations based on a 1-h breakthrough time for commercial film thickness.

HSP alone cannot always correlate barrier properties unless comparisons are limited to solvent molecules with approximately the same size (and shape). This, of course, means that the diffusion coefficients at the reasonably low concentrations expected in better barrier polymers do not vary too greatly from each other. In many cases, satisfactory correlations could only be found when the differences in HSP between the permeant and the barrier polymer were combined with a size (and shape) parameter(s). The molecular volume, V , was found to be a reasonably successful single parameter for this purpose. Printing the correlation data arranged in increasing order of permeant V clearly showed whether the molecular size was important. With regard to the protective ability of the different garments, it was found that, in general, and as expected, the solvents with larger, more complicated structures required much longer times for breakthrough for a given protective membrane type than comparison with other solvents would indicate. Outliers were usually these larger molecular species and permeants with smaller or more linear structure, where diffusion is much more rapid than expected in average comparisons. This size effect is in agreement with what has been known about solvent retention in coatings^{2-4,12,13} and what has been discussed previously. An excellent example of this type of improved correlation is included in Table 13.1 for the breakthrough times of less than 1 h for neoprene rubber used in chemical protective clothing. The first correlation for this material listed in Table 13.1 gives a very poor data fit (0.574). There were 46 out of 66 liquids which had breakthrough times shorter than 1 h. It is clear from closer analysis of the details of the correlation that the outliers are methanol, carbon disulfide, and alkyl alcohol with shorter breakthrough times than predicted and the phthalate plasticizers which have longer breakthrough times than predicted. A perfect fit is found when the molecular volume range of the permeants included in the correlation is abbreviated to between 71 and 172 cc/mol. This eliminates these "outliers." This correlation is based on 39 liquids with breakthrough times of less than 1 h out a total of 50.

The HSP correlations for 1-h breakthrough times for other barrier polymers discussed in Table 13.1 give polymer HSP in the range of those expected from their composition. This includes butyl rubber, Viton® (The Du Pont Company), nitrile rubber, Challenge® 5100 (Chemical Fabrics Corporation, Merrimack, NH), and polyethylene (PE). The thicknesses of all of the films discussed here are those commonly used in chemical protective clothing. HSP correlations of the swelling of Viton are discussed here as well as in Chapter 5 and by Zellers,^{14,15} Evans and Hardy,¹⁶ and by Nielsen and Hansen.¹⁷

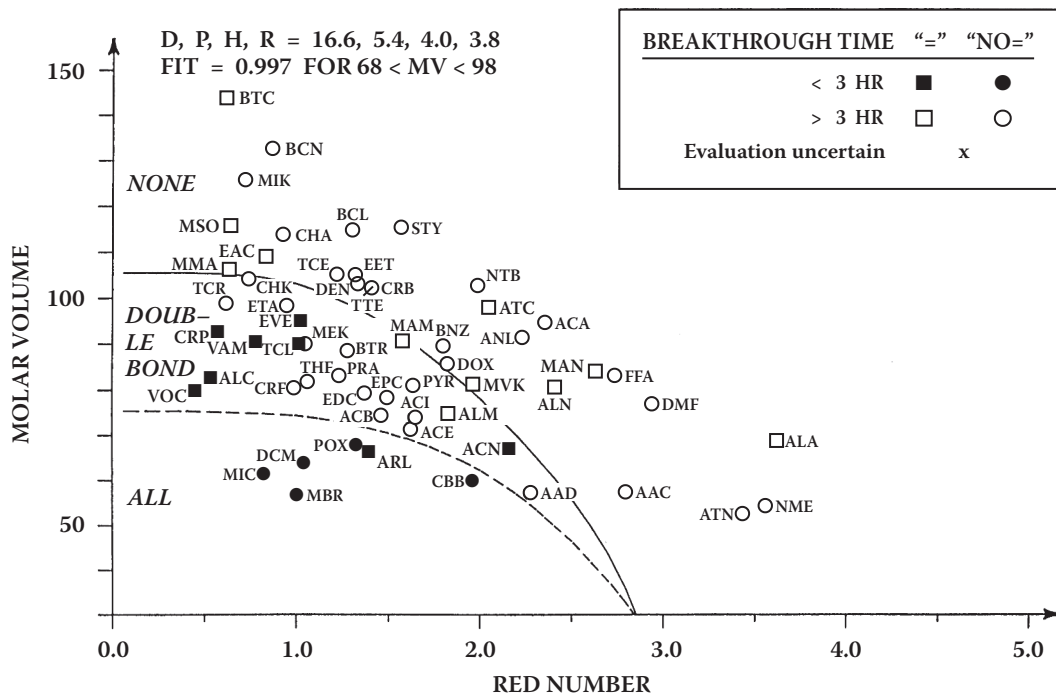


FIGURE 13.2 Graphical method to present HSP correlations. The data are plotted using permeant molar volume vs. RED number. HSP correlation for breakthrough times of less than 3 h in Challenge 5100. Symbols used are explained in Table 13.2. (Reprinted from Hansen, C.M. et al., *The Performance of Protective Clothing: Fourth Volume, ASTM STP 1133*, McBriarty, J.P. and Henry, N.W., Eds., American Society for Testing and Materials, Philadelphia, 1992, 906. With permission. Copyright ASTM.)

The RED number (Chapters 1 and 2) is a key parameter to judge solvent quality. This is given in HSP correlations using Chapter 1, Equation 1.10 as R_a (Chapter 1, Equation 1.9), the difference in HSP between a solvent and a polymer, divided by the radius of the correlating sphere, R_o . The radius of the sphere is actually determined as the difference in HSP of the “worst” good solvent(s) and the HSP for the polymer (which is the center point of the sphere). RED numbers near zero indicate very good solvents (rapid breakthrough). RED numbers increase as the solvent quality decreases. For RED numbers greater than 1.0, the solvent quality is considered “bad,” although swelling may still occur.

Figure 13.2 shows one way to graphically use RED numbers to present data from HSP correlations of permeation phenomena. In this correlation, “good” permeants have breakthrough times of less than 3 h. The data are plotted using V vs. solvent–polymer affinity, i.e., the RED number.¹⁸ The barrier material, Challenge 5100, is a fluoropolymer supported by fiberglass. The abbreviations for the permeants in Figure 13.2 are explained in Table 13.2. This correlation shows that molecules with molar volumes greater than about 100 cc/mol will not have breakthrough times of less than 3 h, regardless of RED number. Molecules with molar volumes greater than about 75 cc/mol require a terminal double bond and lower RED numbers to breakthrough under these conditions. Molecules with still lower molar volumes appear to come through with only a slight dependence on the RED number. The effect with the terminal double bonds clearly indicates the preferential direction of motion for this type of molecule. The molecules in effect worm their way through the barrier polymer.

TABLE 13.2
List of Symbols Used in Figure 13.2

Symbol	Compound	Symbol	Compound
AAC	Acetic acid	EBR	Ethyl bromide
AAD	Acetaldehyde	EDC	Ethylene dichloride
ACA	Acetic anhydride	EET	Diethyl ether
ACB	Acetyl bromide	EIM	Ethyleneimine
ACE	Acetyl chloride	EPC	Epichlorohydrin
ACI	Acetone	ESH	Ethanethiol
ACN	Acrylonitrile	ETA	Ethyl acetate
ALA	Allyl alcohol	EVE	Ethyl vinyl ether
ALC	Allyl chloride	EVK	Ethyl vinyl ketone
ALM	Allyl amine	F12	Dichlorodifluoromethane (Freon 12)
ALN	Allyl cyanide	FFA	Furfural
ANL	Aniline	HXA	Hexane
ARL	Acrolein	MAL	Methanol
ATC	Allyl isothiocyanate	MAM	Methyl acrylate
ATN	Acetonitrile	MAN	Methacrylonitrile
BCM	Bromochloromethane	MAT	Methyl acetate
BCN	Butyl acetate	MBR	Methyl bromide
BNZ	Benzene	MEK	Methyl ethyl ketone
BTC	Butyl acrylate	MES	Methyl sulfide
BTR	Butyraldehyde	MIC	Methyl isocyanate
BUT	Butane	MIK	Methyl isobutyl ketone
BZN	Benzonitrile	MMA	Methyl methacrylate
CAC	Chloroacetylchloride	MSO	Mesityl oxide
CBB	Carbon disulfide	MVK	Methyl vinyl ketone
CBT	Carbon tetrachloride	NEE	Nitroethane
CCF	Dichloromonofluoromethane (Freon 21)	NME	Nitromethane
CHA	Cyclohexylamine	NTB	Nitrobenzene
CHK	Cyclohexanone	POX	Propylene oxide
CLA	Chloroacetone	PRA	Propylamine
CLB	1-Chlorobutane	PYR	Pyridine
CRB	Chlorobenzene	STY	Styrene
CRF	Chloroform	TCE	1,1,2,2-Tetrachloroethylene
CRP	Chloroprene	TCL	Trichloroethylene
DCM	Dichloromethane	TCR	1,1,1-Trichloroethane
DEN	Diethylamine	THF	Tetrahydrofuran
DMF	Dimethyl formamide	TOL	Toluene
DOX	1,4-Dioxane	TTE	Tetrachloroethylene
DSO	Dimethyl sulfoxide	VAM	Vinyl acetate
EAC	Ethyl acrylate	VDC	1,1-Dichloroethylene

Source: Reprinted from Hansen, C.M. et al., *The Performance of Protective Clothing: Fourth Volume, ASTM STP 1133*, McBriarty, J.P. and Henry, N.W., Eds., American Society for Testing and Materials, Philadelphia, 1992, 903. With permission. Copyright ASTM.

SOLUBILITY PARAMETER CORRELATION OF PERMEATION RATES

Permeation rates for different permeants in a polymer can also be correlated to find HSP for the polymer. This is done by dividing a data set into two groups. The “good” solvents will have permeation rates greater than an arbitrarily selected value, and the “bad” solvents will have

TABLE 13.3
HSP Correlations Related to Barrier Polymers

Material	δ_D	δ_P	δ_H	R_o	FIT	G/T
LDPE permeation coefficient 21.1°C	16.3	5.9	4.1	8.2	1.000	26/47
Permeation viable skin ^a	17.6	12.5	11.0	5.0	1.000	4/13
PP swelling ^b	18.0	3.0	3.0	8.0	1.000	13/21
ACLAR® 22 >5 wt% swelling	14.7	3.9	6.7	6.8	1.000	6/26
ACLAR® 22 2%<swelling<5%	18.0	1.0	2.0	4.0	1.000	4/21
Psoriasis scales swelling (Chap. 14)	24.6	11.9	12.9	19.0	0.927	35/50
Viton® swell ^c >10 wt% 20°C	13.1	13.7	3.9	14.7	0.742	36/57
EVOH sol/swell ^d	20.5	10.5	12.3	7.3	0.925	5/24
Polyvinyl chloride swell ^e	18.7	9.7	7.7	6.4	1.000	13/47
Cellophane — >25% swell	16.1	18.5	14.5	9.3	0.955	4/22
PETP chemical resistance (+/- OK) ^f	18.2	6.4	6.6	5.0	0.865	7/34
PA6/PA66 chemical resistance (+/- OK) ^g	17.0	3.4	10.6	5.1	0.984	2/31
PA6/PA66 chemical resistance (+/- bad) ^g	18.9	7.9	11.7	8.0	0.950	9/31

Note: Data fit and the number of good liquids (G) and total number of liquids (T) in the correlations are also indicated. Units are MPa^{1/2}.

^a This correlation is discussed in more detail in Chapter 15 and is based on limited data.²⁰

^b This correlation is based on data by Lieberman and Barbe²² and is discussed in more detail in Chapter 5.

^c This correlation is discussed in Chapter 5. Swelling data is from Reference 23.

^d Ethylene vinyl alcohol copolymer (EVOH), four liquids dissolved and one (morpholine) swelled very strongly.

^e Visual observation of very strong swelling and/or solubility.

^f Polyethylene terephthalate (PETP) chemical resistance based on rather uncertain data²⁴ (see discussion in Chapter 12). Recommendation of uncertain-for-use is considered as acceptable for use. Attacking solvents are within correlating HSP sphere.

^g Polyamide 6/66 chemical resistance based on rather uncertain data²⁴ (see discussion in Chapter 12). Recommendation of uncertain-for-use is used as indicated. Attacking solvents are within the correlating HSP sphere.

Source: From Hansen, C.M., Permeability of polymers, *Pharmaceutical and Medical Packaging* 98, 7.6, 1998. With permission.

permeation rates lower than this value. Such a correlation based on permeation coefficients for various liquids in PE is included in Table 13.3. The permeation coefficient data, (g x mm)/(m² x d), are reported by Pauly¹⁹ for low density polyethylene (LDPE). “Good” solvents are arbitrarily considered as those which have permeation coefficients in these units which are greater than 1.5 at 21.1°C. The parameters reported correlate the data well but are somewhat different from those which might be expected for a polyolefin. Reasons for this are not evident but may include additives in the polymer, local oxidation, or some other local variation in the composition of the polymer. It should be remembered that permeation occurs in the amorphous regions only. This is why high density PE is a better barrier polymer than low density PE; the higher densities are attributable to a higher percentage of crystallinity.

A problem of some concern is the permeation through buried water pipes by chemicals or oil products which somehow reach them, either by general pollution or by gasoline or oil spills. One clearly expects more extensive permeation by chemicals that have HSP not too different from those of the polymer from which the pipe is made, all other things being equal. These pipes are often made from polyolefins.

A HSP correlation has been possible in a very special case of polymer permeability where the barrier polymer is viable human skin.²⁰ This is discussed in more detail in Chapter 15. Human skin is a polymeric barrier with several functions, one of which is to help keep undesirable chemicals out of the body. Some chemicals readily permeate this boundary, and this fact has been used to establish a tentative HSP correlation for the permeation rate of viable human skin. This correlation also has a relation to the HSP correlation for the swelling of psoriasis scales,²¹ which is also discussed in Chapter 15.

SOLUBILITY PARAMETER CORRELATION OF POLYMER SWELLING

Solubility is a major factor in the equation $P = DS$, so correlations of solvent uptake in polymers are important to understand their barrier properties. The correlation for swelling of polypropylene reported in Table 13.3 is based on solvent uptake data reported by Lieberman and Barbe.²² The limit of 0.5% weight gain was arbitrarily set to differentiate “good” solvents from “bad” ones. A different limit might give different parameters. The HSP found in a given correlation of swelling depends on which polymer segments the smaller amounts of permeant prefer to associate with. The predictive ability of the correlation will depend on the number of test liquids used in the study and their given HSP values. How different are the HSP of the test liquids? What are their values compared with the predictions desired? The parameters reported in Table 13.3 for polypropylene seem to accurately reflect what is expected in terms of low polarity and low hydrogen bonding properties for this type of polymer.

As stated previously, a problem of some significance in any study of solvents at low concentrations in polymers is that the smaller amounts of solvent relative to the polymer can lead to preferential association of solvent with those local regions/segments/groups in the polymer that have energies (HSP) most similar to their own. Like seeks like. These local regions may not necessarily reflect the same affinities as the polymer as a whole, such as are indicated by the totally soluble-or-not approach most commonly used in HSP evaluations. These local association effects can influence results on swelling studies at low solvent uptakes in both good and bad solvents, for example. Copolymers, such as Viton, are particularly susceptible to this problem. Swelling data for Viton²³ are correlated by the HSP values included in Table 13.3. A poor data fit can be anticipated when a single HSP sphere is used to describe what should be represented by (at least) two overlapping HSP spheres (see also Figure 13.3). Zellers^{14,15} also had difficulty correlating the swelling of Viton. Other types of studies carried out at low solvent concentrations can also be influenced by this segregation/association phenomena. An extension of this type of situation can be cited in the tendencies of water to associate with itself as well as with local hydrophilic regions within polymers. The amount of water taken up at equilibrium is not reflected by an overall HSP correlation of polymer solubility or swelling. As little as 1% of hydrophilic additive can effectively destroy the water barrier properties of a polymer film, but this small amount cannot be measured in swelling or solubility studies leading to HSP correlations. This fact, among other things, has made simple predictions of the behavior of water very difficult.

Correlations of polymer solubility and swelling have led to several of the HSP data sets reported in Table 13.3 (see also the data reported in Chapter 5). The HSP correlations for chemical resistance based on data of the acceptable-for-use or recommended/not recommended type are not as reliable as those usually found for solubility and swelling where a suitably large number of liquids are used in the testing. The reasons for this are discussed in depth in Chapter 12. The data used in the chemical resistance correlations reported in Table 8.3 were taken from Reference 24.

ACLAR[®] 22 Bimodal Uptake HSP Correlations

Uptake	δ_D	δ_P	δ_H	R	FIT	
5 - 10 %	14.7	3.9	6.7	6.8	1.000	●
2 - 5 %	18.0	1.0	2.0	4.0	1.000	■
> 10 %	Trichloroethylene within both					×

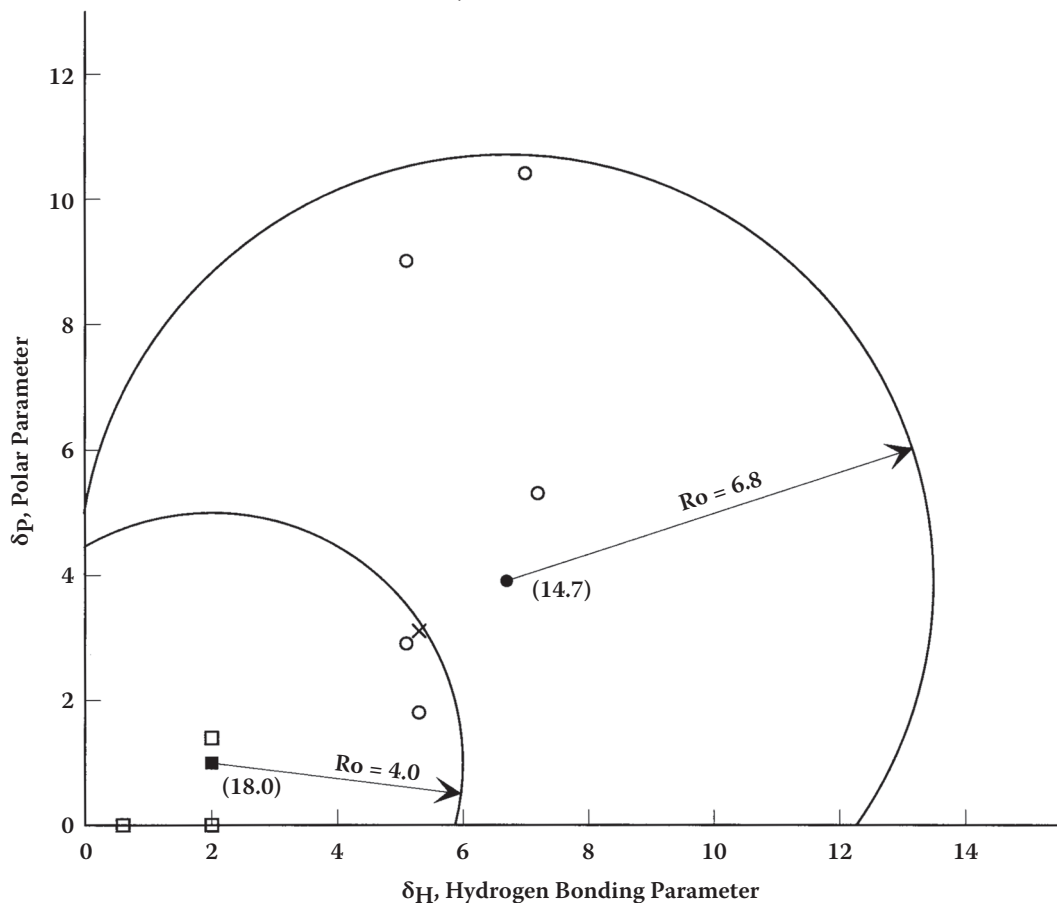


FIGURE 13.3 Bimodal HSP correlation(s) for uptake of liquids in ACLAR[®] 22. Trichloroethylene uptake is the largest among the test solvents because it is the only solvent found within both regions. It has RED numbers of 0.999 for the >5% correlation and 0.978 for the correlation of uptake between 2 and 5%. As the data fit is 1.0 for both correlations, other sets of parameters can also give data fits of 1.0. However, the numbers are approximately correct. Units are MPa^{1/2}.

SOLUBILITY PARAMETER CORRELATION OF PERMEATION COEFFICIENTS FOR GASES

Gases can also be assigned δ_D , δ_P , and δ_H parameters. For strictly nonpolar gases, the values of δ_P and δ_H will be zero, but other gases, such as carbon dioxide, hydrogen sulfide, etc., will have significant values for all three parameters. Table 13.4 gives the δ_D , δ_P , and δ_H parameters for a number of gases. It is not surprising that there are HSP correlations of permeation coefficients for gases in different polymers as a function of their solubility parameter differences. One such correlation using the total solubility parameter has been given by König and Schuch,²⁵ who showed

TABLE 13.4
HSP for Common Gases of
Interest in Permeation
Phenomena

Gas	δ_D	δ_P	δ_H
Water	15.5	16.0	42.3
Ammonia	13.7	15.7	17.8
Chlorine	17.3	10.0	0.0
Sulfur dioxide	15.8	8.4	10.0
Carbon dioxide ^a	15.7	6.3	5.7
Carbon monoxide	11.5	4.9	0
Ethane	15.6	0	0
Ethylene	15.0	2.7	2.7
Helium	1.0	0	0
Hydrogen	5.1	0	0
Hydrogen sulfide	17.0	6.0	10.2
Methane	14.0	0	0
Nitrogen oxide	11.5	20.0	0
Nitrogen	11.9	0	0
Nitrous oxide	12.0	17.0	0
Oxygen	14.7	0	0
Acetylene	14.4	4.2	11.9

Note: Units are MPa^{1/2}.

^a Values changed from 1st Edition. See Chapter 10 Addendum.

that the better barrier polymers for oxygen, i.e., those with low oxygen permeation coefficients, were those whose solubility parameters were most different from the solubility parameters of oxygen. The better barrier polymers for oxygen include polyacrylonitrile and polyvinyl alcohol, whereas the poorer barriers include polyolefins and polytetrafluoroethylene (PTFE). The amounts of gases dissolved at low pressures are usually low, and constant diffusion coefficients are expected. This may not be true at higher pressures where solubility parameters for the gases increase more rapidly than those of the polymers and polymers can absorb them to a greater extent. See Chapter 10.

An example of how HSP principles can be applied to interpreting the behavior of gas barrier films can be found in the performance of poly(chlorotrifluoroethylene). The data on which the example is based are taken from the commercial literature supplied by Allied Signal concerning their barrier films under the tradename of ACLAR®.²⁶ These films are excellent barriers for water and oxygen, and various laminating possibilities exist, including polyethylene, polyvinyl chloride, and polyethylene terephthalate. The barrier properties of films made from this material are not nearly as good for carbon dioxide as they are for nitrogen or oxygen. A contributing factor in this is that the HSP of the polymer is somewhat different from the HSP of oxygen and nitrogen, but close to the HSP of carbon dioxide. A HSP correlation for the swelling of ACLAR 22 to greater than 5 wt% is included in Table 13.3. The RED numbers for water, nitrogen, oxygen, and carbon dioxide based on this correlation are 5.5, 1.4, 1.1, and 0.48, respectively. Nitrogen has slower permeation than oxygen, and both are much slower than carbon dioxide, in general agreement with this ranking. One might have expected the permeation rate of carbon dioxide to be lower than that of nitrogen and oxygen as it is a larger molecule, but the enhanced solubility of carbon dioxide in the polymer overrides this expectation.

Figure 13.3 shows that there are two distinct spherical characterizations possible for ACLAR 22. The first of these, as discussed earlier, is for liquid uptake to greater than 5% by weight. The second of these is for uptake between 2 and 5% by weight. This second correlation is also reported in Table 13.3. There is one liquid in the data which is common to both of the HSP regions pictured in Figure 13.3. This is trichloroethylene (which was assumed to be a good solvent in both of the perfect correlations in spite of being absorbed to over 10% by weight). Even though trichloroethylene has high RED numbers in both correlations, this solvent is absorbed more than any of the other solvents tested because of this property. The primary uptake region has HSP that might be expected from a fluoropolymer, whereas the secondary HSP region is what might be expected from a chlorinated species. Such secondary regions can potentially allow higher permeation rates and greater absorption of unpredictable materials based on a single HSP correlation. Searching a database of solvents, plasticizers, aromatic compounds, etc., would show which of these could behave in an unexpected manner.

Sometimes an indirect approach allows prediction of the uptake of a gas in a polymer. This involves determining the uptake of the gas in a liquid having solubility parameters that are similar to those of the polymer. This approach expands the usefulness of gas–liquid equilibrium data. Correlations of gas–liquid solubility with the solubility parameter are included in Figure 13.4 for the equilibrium values for water²⁷ and in Figure 13.5 for the equilibrium values for nitrogen.²⁸ The quantity P^*y/x is given by the total pressure, P^* , the mole fraction in the gas phase, y , and the mole fraction in the liquid phase, x . The abbreviations used in Figure 13.5 are explained in Table 13.5.

The solubility parameters for gases not found in Table 13.4 may be found in standard references.^{29–31} HSP for gases can be calculated using the procedures outlined in Chapter 1 with the special figure for gases included in Chapter 18 (Figure 18.2). There can be problems of dividing the total cohesive energy into three parts. Sulfur trioxide is a good example of how one cannot come further in dividing the energy of vaporization into components without experimental data. The techniques of Chapter 3 have not been explored in this context however. The total (Hildebrand) solubility parameter, δ_t , indicated from the total energy of vaporization is 31.3 MPa^{1/2}. δ_D found by the usual techniques is 15.6 MPa^{1/2}. This leaves a residual corresponding to a solubility parameter value of 27.2 MPa^{1/2} to be distributed between permanent dipole and hydrogen bonding (electron transfer) effects. There is no dipole moment, and neither is there a hydrogen atom. This clearly requires experimental data to resolve the distribution of the energy of vaporization into components for all of these effects, even if there are supporting estimates from the techniques of Chapter 3.

It might be noted that the scale in Figure 13.4 for the uptake of water in various liquids is exponential with data covering almost five decades in concentration. The phenomena correlated in this figure confirm the expectation that nonpolar polymers, with solubility parameters far different from those of water, will be good barrier polymers for water because of low water solubility. This is generally true, of course. As mentioned earlier, such polymers include the polyolefins as well as chlorinated and fluorinated polymers. These comments and generalities are not necessarily valid for polymers containing additives. Depending on the nature of the additive and the amounts present, some of these can totally change the barrier performance of the base polymer.

LAMINATES

Laminated barrier polymer systems are designed to make the best use of the properties of each of the individual layers, as well as to optimize cost with performance. The most common type has a polyolefin on the exterior surfaces to protect the inner barrier polymer from water. These interior barrier polymers often have relatively high solubility parameters, such as ethylene vinyl alcohol copolymers (EVOH), polyamides (PA), or polyethylene terephthalate (PET). If the inner barrier polymer takes up water, it will be plasticized, and its barrier properties will be reduced. A polyolefin

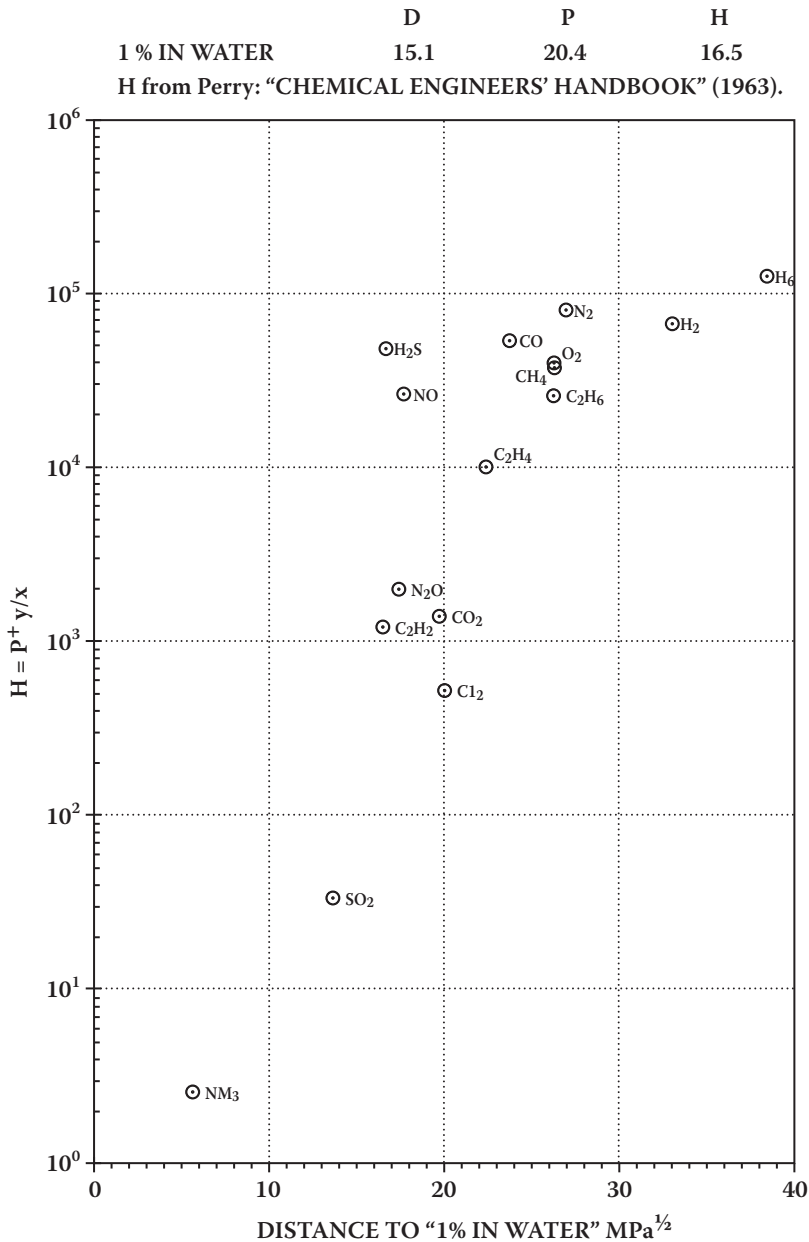


FIGURE 13.4 HSP correlation of gas–water equilibrium data using water HSP values found with a correlation using a limit of >1% liquid soluble in water as a “good” solvent,²¹ and gas–water equilibrium data from Perry et al.²⁷ P^* is the total pressure, y is the mole fraction in the gas phase, and x is the mole fraction in the liquid phase. (From Hansen, C.M., *Dan. Kemi*, 73(8), 21, 1992. With permission.)

laminated to such a potentially water-sensitive barrier film can significantly delay this uptake and loss of barrier properties and maintain reasonable costs. Depending on the performance desired, various combinations of laminates can be systematically designed using HSP considerations as one of the design parameters.

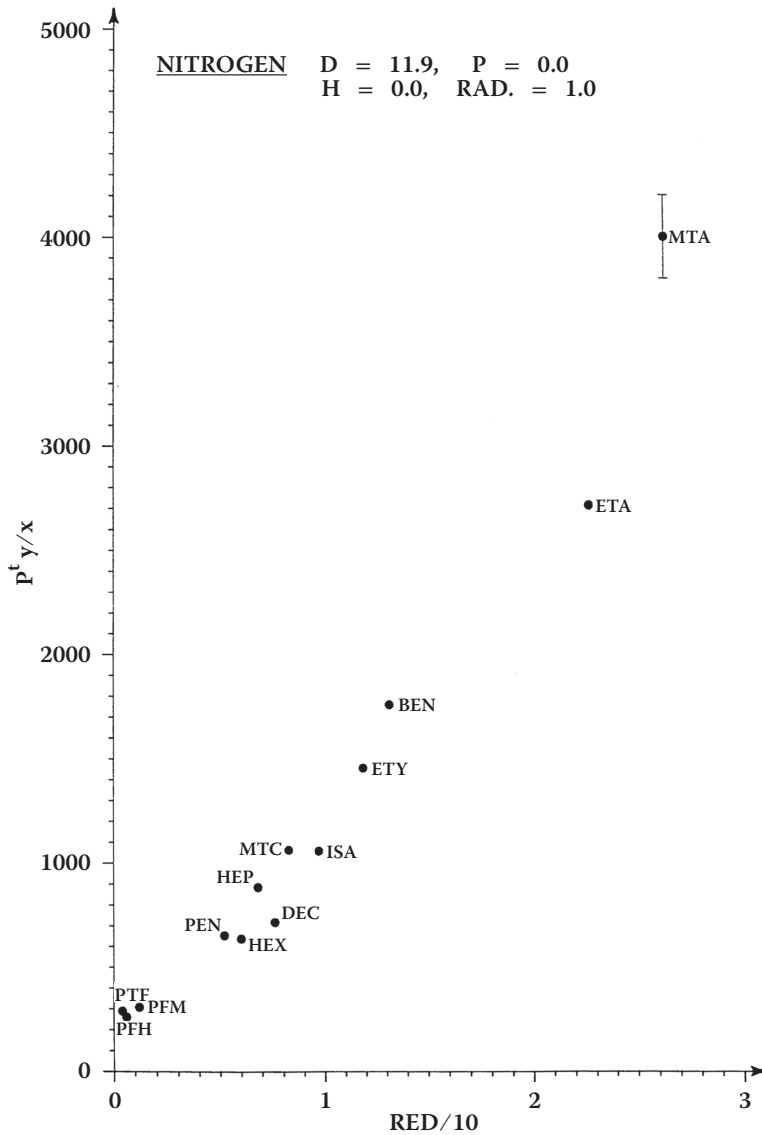


FIGURE 13.5 HSP correlation of nitrogen–liquid equilibrium data at temperatures near 25°C and low pressure. P^* is the total pressure, y is the mole fraction in the gas phase, and x is the mole fraction in the liquid phase. (From Hansen, C.M., *Dan. Kemi*, 73(8), 20, 1992. With permission.)

GENERAL CONSIDERATIONS

HSP correlations have been possible for many phenomena where differences in behavior on contact with different solvents have been studied. The HSP correlations are preferably based on systems in thermodynamic equilibrium, although the correlations presented previously on breakthrough times are an exception to this. These correlations were possible because of the exceptional dependence of the permeation phenomena on the amount of permeant being dissolved.

There is a strong dependence of the diffusion coefficient of permeants in polymers on their size and shape. This can clearly affect HSP correlations of permeation coefficients, as two permeants with identical HSP will have different D if their sizes and shapes are significantly different. This

TABLE 13.5
Key to Symbols Used in Figure
13.5

Symbol	Compound
PFH	Perfluoroheptane
PTF	Perfluorotributylamine
PFM	Perfluoromethylcyclohexane
PEN	Pentane
HEX	Hexane
HEP	Heptane
MYC	Methyl cyclohexane
ISA	Isobutyl acetate
ETY	Ethyl acetate
BEN	Benzene
ETA	Ethanol
MTA	Methanol

differential in diffusion rate based on solvent size and shape can also give apparent errors in HSP correlations of polymers for their chemical resistance, for example, where not enough exposure time has been allowed for attainment of equilibrium. This is clearly a problem in the determination of equilibrium degree of swelling and low amounts of uptake. This problem has also been found, for example, for exposures of thick samples (3 to 4 mm) of rigid polymers used for tensile testing after solvent exposure for given times. Crystalline polymers also have a tendency to be more readily soluble in solvents with lower V , all other parameters being equal, but this is explained by thermodynamic considerations rather than a relatively faster diffusion process. In all of these cases, the majority of the outliers in the correlations are the test liquids with higher V . The time required for attainment of equilibrium with the larger diffusing molecules can be so long as to be prohibitive for their reasonable inclusion in HSP correlations. It is suggested that diffusion rates be carefully considered when liquids with very high V are outliers in HSP correlations. Neglecting such data for the sake of a correlation can be justified, but this is a warning that the diffusion process for these liquids has not yet achieved equilibrium and that the effects of such liquids can be expected to be more severe at still longer times than those used in the study. HSP correlations can be used in this way to find those exposure liquids which have not reached equilibrium at the exposure time chosen for evaluations.

CONCLUSION

Successful HSP correlations for the permeation and solubility behavior of selected barrier polymers have been presented to demonstrate the use of simple principles to arrive at optimum barrier systems, as well as to determine reliable HSP for the polymers studied. Selection of polymer–permeant combinations with widely different solubility parameters will ensure low solubility of the permeant in the polymer. This reduces the concentration gradient and prevents significant self-plasticization of the polymer. The self-plasticization leads to concentration-dependent diffusion coefficients, an effect which becomes more significant with increasing amounts of permeant being dissolved, i.e., a closer HSP match. See Chapter 16 for more discussion of diffusion in polymers.

HSP correlations have been presented for breakthrough times in chemical protective clothing, permeation rates in barrier polymers, and swelling of various types of polymers. Both gases and liquids are treated.

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