

# A collection of kinetic data for the diffusion of organic compounds in polyolefins

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A comprehensive collection of kinetic data on the diffusion of organic compounds in polyolefins is contained in tables for low density polyethylene, high density polyethylene, polyisobutylene, polypropylene, hydrogenated polybutadiene, poly(4-methylpentene-1), ethylene-propylene copolymers, and self-diffusion of polyolefins. Diffusion constants for over 250 polymer-migrant entries at temperatures from  $-30^{\circ}$  to  $190^{\circ}\text{C}$ , activation energies and pre-exponential factors for the diffusion process and parameters for the concentration dependence of the diffusion constant are included. A special feature of this compilation is an extensive section of annotated references. This includes: (1) as complete a characterization of each polymer and migrant as is possible. (2) a description of the experimental methods used to determine the diffusion constants, and (3) the assumptions made, equations utilized and calculations performed to obtain the data in the tables. The tables exhibit remarkable consistencies, considering the great variations in diffusion constants which can be brought about by thermal, mechanical, and solvent action. These consistencies lend hope that useful correlations may be developed from these data.

**Keywords** Additives; Arrhenius parameters; concentration dependence; diffusion constants; migrants; organic vapours; polyethylene; poly(isobutylene); polyolefins; polypropylene; self-diffusion

## INTRODUCTION

Most of the literature on the kinetics of diffusion of organic compounds in polyolefins is reviewed in this paper and kinetic constants are tabulated. The summaries of each of the references feature information on the characterization of the polymers and diffusing materials as well as on experimental methods used and assumptions made in modelling and calculating the tabulated data.

There are many problems involved in an attempt to compare and interpret experimental data on diffusion in polymers. These difficulties stem both from the dependence of the morphological character of the polymer matrix upon its physical and chemical history and from the complex time and concentration dependent physical and chemical interaction between the diffusing substance and the polymer matrix through which it is diffusing. Thus it is very difficult, if not impossible, to fully characterize the system or adequately model the process taking place.

In spite of, or perhaps because of, the above difficulties, there is a definite need for this compilation on both theoretical and practical grounds. Polyolefins are the chemically simplest and the best understood morphologically of the vinyl polymers and therefore are the most amenable to correct theoretical modelling. It is hoped that trends and irregularities in these data will inspire the development of improved and more realistic models for the diffusion process. Also, polyolefins are the most widely used polymers in commerce, especially in the food packaging, chemical container and transportation industries. This paper may serve both as a data source for these areas and as a basis for the development of empirical

equations for predicting migration into and out of packaging and containers.

## RATIONALE FOR THE FORMAT OF THE TABLES AND THEIR ANNOTATED REFERENCES

An attempt was made to avoid a selection of the data based on subjective decisions as to the quality of methods of measurement, the data itself, or the models used to describe the diffusion process. However, it is appropriate to give an explanation for the choices made in the selection of the form in which the data are presented.

In the first place, and of somewhat trivial importance, the term 'migrant' has been used in this paper for the lower molecular weight species, rather than the term 'diffusant'. The use of 'migrant' is commonplace in the literature on polymers and 'migrant' possesses the advantage of a more realistic connotation. That is, 'diffusion' suggests the purely physical process of a gas slipping through a matrix due to its Brownian motion while 'migration' gives the image of dwelling in the system and hopping from site to site. The purely physical process is belied by the high activation energies encountered in most of these processes.

The two guiding principles in selecting the format for the tables were: the presentation of as much useful and comparable data as possible, and the inclusion of as much information as possible on the materials, methods and calculations so as to allow rational judgments by the reader as to the similarities and distinctions among the entries.

Two mathematical models, Fick's Law and the Arrhenius Equation, were evoked in order to present the data in a coherent and comparable manner.

#### Fick's Law of diffusion

Diffusion of a nonreactive migrant through a fixed isotropic polymer matrix due to its random (Brownian) motion is described by Fick's first law:

$$F = -D\partial c/\partial x \quad (1)$$

where  $F$  is the rate of mass transfer per unit cross section,  $c$  is the concentration of migrant and  $x$  is the direction coordinate normal to the cross section.  $D$  is defined as the diffusion constant. It is, of course, a rate constant and usually in units of  $\text{cm}^2 \text{s}^{-1}$ . For most polymer-migrant systems in which diffusion is occurring at conveniently measurable rates, its values range several orders of magnitude about  $10^{-8} \text{ cm}^2 \text{ s}^{-1}$  or  $1 \mu\text{m}^2 \text{ s}^{-1}$  in SI units. Due to the many factors which contribute to deviations from the ideal conditions assumed in the formulation of equation (1), other diffusion coefficients have been defined and are used to model appropriate experimental data. These will be defined later. The complete solutions of equation (1) and Fick's Second Law (equation (6) in Discussion section) are dealt with by Crank (1975) where a large variety of boundary conditions are applied. Also, methods of incorporating deviations from Fick's laws in cases in which  $D$  is time and/or concentration dependent and the definition and measurement of variable diffusion coefficients for these cases are dealt with by Crank (1975). This reference is the basis for the discussion of methods and calculations in the annotated references herein, and the relevant sections and equations by Crank (1975) are given whenever applicable.

#### Arrhenius equation

The Arrhenius equation as applied to diffusional kinetics is given in

$$D = A \exp(-E/RT) \quad (2)$$

equation (2) where  $A$  is the pre-exponential factor,  $E$  is the energy of activation,  $R$  is the gas constant and  $T$  is the absolute temperature. This equation was used to model the temperature dependence of the diffusion constant whenever values for  $D$  were given at two or more temperatures except for a few cases where gross deviations from linearity of  $\log D$  vs.  $1/T$  curves indicated that the model was not applicable.

Since the range of temperatures at which the diffusion measurements were made lies well above the glass transition temperature of the polymers, the adherence to Arrhenius-type temperature dependence is not surprising. It is mainly at temperatures below that of the glass transition that lack of constancy of  $E$  and  $A$  are common.

## DIFFUSION TABLES

### General comments on the tables

The data were divided into eight tables according to types of polymer substrate, *Table 1*: Low density polyethylene; *Table 2*: High density polyethylene; *Table 3*: Polyisobutylene; *Table 4*: Polypropylene; *Table 5*: Hydrogenated polyisobutadiene; *Table 6*: Poly(4-methyl

pentene-1); *Table 7*: Ethylene-propylene copolymers; and *Table 8*: Self diffusion of polyolefins.

All of these tables have most features in common. The migrants are listed in the first column in order of ascending molecular weights which are given in the second column. (This is not meant as an effort to correlate the magnitude of the diffusion coefficient inversely with the molecular weight of the migrant as obviously other factors, both geometrical and chemical, affect diffusion rates.)

A symbol indicating type of diffusion constant is given in the third column of the tables. The significance of these symbols is discussed in the annotated references and more completely by Crank (1975).

$\bar{D}$  is the mean value or average diffusion constant over a concentration range.

$\bar{D}$  (pressure) is the diffusion constant for a gaseous migrant measured at or extrapolated to the indicated pressure.  $D^V$  is the interdiffusion coefficient.  $D$  is the self diffusion coefficient.  $D^*$  is the self diffusion coefficient for an isotopically labelled migrant.

$D_{c \rightarrow 0}$ ,  $\bar{D}_{c \rightarrow 0}$ ,  $D_{c \rightarrow 0}^*$  are diffusion constants from extrapolating diffusion constants at differing concentrations to zero concentration, or diffusion constants found to be concentration independent at low concentrations. (In some of the references, this latter assumption appears to be little more than a pious hope rather than a fact based upon scientific evidence.)

$D_{V \rightarrow 0}$ ,  $D_{V \rightarrow 0}^*$  are diffusion constants obtained from extrapolation of diffusion coefficients at differing volume fraction of migrant to zero volume fraction.

Two types of experimentally determined diffusion constants are given special notation due to their lack of consistency with those from other techniques, viz:

$D_{\text{PVC}}$  is the diffusion coefficient determined for diffusion from a 35 migrant/65 poly(vinylchloride) sheet into a polymer sheet (see Thinius (1964)).

$D_{\text{gc}}$  is the diffusion coefficient determined from inverse gas chromatography.

All of the tables give the diffusion constant for the lowest temperature exactly divisible by ten (or for 25°C) in the temperature range over which source data are available. When values at two or more temperature were available, and the Arrhenius equation fit these data in a reasonable manner, the value for the diffusion constant was calculated for the lowest temperature from the Arrhenius parameters,  $A$  and  $E$ . In many cases, the value was obtained directly from Arrhenius curves or Arrhenius parameters in the data source. Single datum points for diffusion constants were either entered directly into the table or extrapolated to a temperature of the nearest multiple of ten by assuming a reasonable value for the activation energy. In several cases, where sufficient data were available both below and above the melting region of the polymer, separate Arrhenius parameters were calculated for the semicrystalline and liquid-state temperature regions. The above calculations are described for each case in the appropriate annotated reference.

Extended tables giving the values of the diffusion constants at ten degree intervals over the entire experimental ranges may be obtained from the author. Only the diffusion constant for lowest temperature of the range is given for each migrant in the tables so as to reduce their size. Values of the diffusion constant can be

Table 1 Low density polyethylene

Migrant	Mol. wt.	Type diffusion constant	Diffusion Constant* ( $10^8 \text{ cm}^2 \text{ s}^{-1}$ ) (Temperature range °C)	Log A	(kJ mol <sup>-1</sup> ) E	Annot. ref.
Methane	16.0	$\bar{D}$	7.7 (10, 50)	1.28	45.6	1
Methane	16.0	$\bar{D}$	16.3 (20, 50)	1.56	49.0	2
Methane	16.0	$\bar{D}$ (1 Atm)	250 (30)	—	—	3
Methane	16.0	$D_{g.c.}$	~0.5 (40), ~2 (70)	—	—	4
Methane	16.0	$D$ (1 Atm)	3500 (140) 5600 (190)	—	—	5
Formaldehyde	30.0	$D_{g.c.}$	2.8 (40)	—	—	6
Ethane	30.1	$D_{C \rightarrow 0}$	0.028 (-30, 30)	3.33	60.0	7
Ethane	30.1	$\bar{D}$ (2.9 Atm)	1.76 (0, 25)	0.63	43.9	8
Ethane	30.1	$\bar{D}$	0.54 (0, 50)	4.03	64.4	9a
Ethane	30.1	$\bar{D}$	0.80 (0, 50)	2.11	53.6	9b
Ethane	30.1	$\bar{D}$	2.3 (10, 50)	2.21	53.6	1
Ethane	30.1	$\bar{D}$	5.4 (25)	—	—	10
Ethane	30.1	$\bar{D}$ (1 Atm)	26.5 (30)	—	—	3
Allene	40.1	$\bar{D}$	3.8 (10, 50)	1.74	49.8	1
Propylene	42.1	$\bar{D}$	2.0 (10, 50)	2.73	52.3	1
Propane	44.1	$\bar{D}$	1.05 (10, 50)	2.26	55.6	1
Isobutylene	56.1	$D_{C \rightarrow 0}$	0.102 (-10, 30)	3.34	63.9	11a
Penetane	72.2	$\bar{D}$	0.98 (25, 50)	5.02	73.4	9a
2,2-Dimethylpropane	72.2	$\bar{D}$	0.20 (25, 50)	6.50	86.8	9a
Benzene	78.1	$\bar{D}_{C \rightarrow 0}$	0.19 (0)	—	—	11a
Benzene	78.1	$D_{g.c.}$	0.82 (25)	—	—	12a
Benzene	78.1	$\bar{D}_{C \rightarrow 0}$	1.43 (25, 30)	2.63	65.5	13
Benzene	78.1	$D_{C \rightarrow 0}$	1.32 (25, 40)	3.84	66.9	14
Benzene	78.1	$D_{C \rightarrow 0}$	1.18 (25, 50)	3.36	64.4	15
Benzene	78.1	$D_{g.c.}$	~0.5 (40), ~1 (70)	—	—	4
Benzene	78.1	$D_{V \rightarrow 0}$	13.2 (50)	—	—	16
Hexene-2	84.2	$D_{C \rightarrow 0}$	0.83 (25, 50)	1.45	54.4	15
Cyclohexane	84.2	$D_{C \rightarrow 0}$	0.48 (25, 50)	2.38	61.1	15
n-Hexane	86.2	$\bar{D}_{C \rightarrow 0}$	0.120 (0, 30)	4.41	69.7	11a
n-Hexane	86.2	$\bar{D}_{C \rightarrow 0}$	0.015 (0)	—	—	11b
n-Hexane	86.2	$D_{C \rightarrow 0}$	1.35 (25, 40)	-0.89	45.5	13
n-Hexane	86.2	$D_{C \rightarrow 0}$	1.05 (25, 40)	1.72	55.4	14
n-Hexane	86.2	$D_{C \rightarrow 0}$	0.64 (25, 50)	3.24	65.3	15
3-Methylpentane	86.2	$D_{C \rightarrow 0}$	0.49 (25, 50)	2.54	61.9	15
2,2-Dimethylbutane	86.2	$D_{C \rightarrow 0}$	0.34 (25, 50)	2.89	64.9	15
Chlorodifluoromethane	86.5	$D$ (1 Atm)	4300 (190)	—	—	17
p-Dioxane	88.1	$D_{C \rightarrow 0}$	0.51 (25, 50)	4.90	75.3	15
Ethylacetate	88.1	$\bar{D}$	1.39 (40)	—	—	18
Bromomethane	95.0	$\bar{D}_{C \rightarrow 0}$	0.87 (0, 30)	1.84	51.8	11c
Bromomethane	95.0	$\bar{D}_{C \rightarrow 0}$	2.9 (0)	—	—	11b
Bromomethane	95.0	$\bar{D}$ (600 mm)	3.2 (0, 60)	0.41	42.4	19
n-Heptane	100.2	$D_{C \rightarrow 0}$	1.22 (25, 30)	-1.09	44.7	13
p-Xylene	106.2	$\bar{D}$	45 (25, 50)	-0.41	33.9	20
o-Xylene	106.2	$\bar{D}$	14.3 (25, 50)	1.60	48.2	20
n-Octane	114.2	$D_{C \rightarrow 0}$	0.44 (25, 50)	2.42	61.5	15
2,2,4-Trimethylpentane	114.2	$D_{C \rightarrow 0}$	6.5 (50)	—	—	21a
2,2,4-Trimethylpentane	114.2	$D_{C \rightarrow 0}$	11.3 (50)	—	—	21b
2,2,4-Trimethylpentane	114.2	$D_{C \rightarrow 0}$	21 (50)	—	—	21c
Tetralin	132.2	$D_{g.c.}$	9.5 (120, 140)	0.027	41.1	22
cis-Decalin	138.3	$D_{g.c.}$	7.3 (120, 130)	-1.98	38.9	22
trans-Decalin	138.3	$D_{g.c.}$	8.4 (120, 140)	-2.30	36.0	22
n-Decane	142.3	$D_{C \rightarrow 0}$	0.48 (25, 50)	3.34	66.5	15
n-Decane	142.3	$D_{g.c.}$	0.42 (30, 80)	—	—	12
Carbon tetrachloride	153.8	$D_{C \rightarrow 0}$	0.37 (25, 50)	7.44	82.8	15
Carbon tetrachloride	153.8	$D_{g.c.}$	~0.3 (50), ~0.2 (80)	—	—	4
n-Dodecane	170.3	$D_{g.c.}$	7.4 (120, 130)	-2.59	34.2	22
Tert-butyl-4-hydroxyanazole	180.2	$D_{g.c.}$	6.8 (140, 170)	-1.96	41.2	22
n-Tetradecane	194.4	$D_{g.c.}$	1.16 (130, 170)	+0.81	67.5	12
2,4-Dihydroxy benzophenone	214.2	$D_{C \rightarrow 0}$	0.20 (40, 70)	4.21	77.3	23
2,5-Tertbutyl-4-hydroxy-toluene	220.3	$D_{C \rightarrow 0}$	3.1 (70, 90)	0.83	54.8	24
2,5-Tertbutyl-4-hydroxy-toluene	220.3	$D_{g.c.}$	4.3 (140, 170)	-2.52	38.3	22
n-Hexadecane	226.4	$D_V$	700 (100)	—	—	25
Tetradecane-amide	227.4	$D_{C \rightarrow 0}$	280 (120)	—	—	26
2-Hydroxy-4-methoxybenzophenone	228.2	$D_{C \rightarrow 0}$	4.4 (70, 90)	0.28	50.2	27
n-Octadecane	254.5	$D_{C \rightarrow 0}$	0.53 (30, 60)	6.35	84.9	63
n-Octadecane	254.5	$D_{C \rightarrow 0}$	4.0 (40, 90)	0.43	46.9	28
Hexadecane	255.4	$D_{C \rightarrow 0}$	243 (120)	—	—	26
2-Hydroxy-4-butoxybenzophenone	270.3	$D_{C \rightarrow 0}$	2.1 (40, 60)	2.76	68.6	27
Dibutylphthalate	278.3	$D_{PVC}$	12N5 (20, 70)	4.73	93.5	29
Paraffin	~325.0	$D_{V \rightarrow 0}$	0.32 (90)	—	—	30
Octadecane-amide	283.4	$D_{C \rightarrow 0}$	0.35 (90, 140)	-1.96	28.0	26
2-Hydroxy-4-octoxy benzophenone	326.4	$D_{C \rightarrow 0}$	0.045 (40, 70)	2.52	65.0	31
2-Hydroxy-4-octoxy benzophenone	326.4	$D_{C \rightarrow 0}$	2.1 (70, 90)	0.92	56.5	27

<i>n</i> -Octadecyl-diethanol amine	357.6	$D_{C \rightarrow 0}$	0.21 (20, 100)	0.50	51.5	32
4,4'-Thiobis (3-methyl-6-tertbutylphenone)	358.5	$D_{C \rightarrow 0}$	0.198 (40, 70)	3.87	75.3	60
Tricresyl phosphate	368.4	DPVC	41N6 (40, 70)	14.9	163.0	29
2-Hydroxy-4-dodecoxybenzophenone	382.5	$D_{C \rightarrow 0}$	1.62 (70, 90)	1.13	58.6	27
Bis(2-ethylhexyl)phthalate	390.6	DPVC	36N6 (20, 70)	13.19	144.0	29
Ceresin	~450.0	$D_{V \rightarrow 0}$	56.0 (120, 130)	-2.22	30.3	33
2-Hydroxy-4-octadecoxybenzophenone	466.7	$D_{C \rightarrow 0}$	1.47 (70, 90)	0.83	56.9	27
Didodecyl 3,3'-thiodipropionate	514.8	$D_{C \rightarrow 0}$	2.3 (60, 100)	0.50	51.9	32
Ceresin	~525.0	$D_V$	21.0 (120, 130)	19.17	194.0	25
1,1,3-Tri[2-methyl-4-hydroxy-5 ( <i>t</i> -butyl)phenyl]butane	544.8	$D_{C \rightarrow 0}$	0.50 (60, 100)	-0.30	51.0	32
Ceresin	~600.0	$D_{V \rightarrow 0}$	26.0 (100, 120)	-0.73	41.8	33
Doconsanyl doconsanate	649.1	$D_{C \rightarrow 0}$	0.154 (40, 100)	6.84	93.8	26
Doconsanyl doconsanate	649.1	$D_{C \rightarrow 0}$	50.0 (110, 160)	-2.19	30.4	26
Tetakis[methylene-3(3',5'-di-tert- butyl-4-hydroxyphenyl)propionate] methane	1177.0	$D_{C \rightarrow 0}$	1.13 (50, 80)	-0.21	54.1	60
Polyethylene	2000.0	$D_V$	0.55 (120, 130)	35.41	329.0	25
Linear polyethylene	3600.0	$\bar{D}$	3.0 (180)	-	-	26
Linear polyethylene	4600.0	$\bar{D}$	1.86 (180)	-	-	26
Linear polyethylene	11 000.0	$\bar{D}$	0.34 (180)	-	-	26
Linear polyethylene	17 000.0	$\bar{D}$	0.150 (180)	-	-	26
Linear polyethylene	23 000.0	$\bar{D}$	0.081 (180)	-	-	26

\* Diffusion constant calculated for the lowest temperature of the range ( $aa/Nb = aa \times 10^{-b}$ )

calculated for any temperature by substitution of appropriate values of  $\log A$  and  $E$  into the Arrhenius equation. The precision of measurement of the diffusion constants is unknown in most cases and the significant figures used to represent their values are arbitrary.

Each of the tables contains columns listing the logarithm to the base ten of the pre-exponential factor,  $\log A$ , and the energy of activation,  $E$ , in  $\text{kJ mol}^{-1}$ .

The number in the final column of each table refers to the section in the annotated references which describes the experimental details and how the data in that row were obtained.

#### Comments on specific tables

The data on diffusion in polyethylene have been separated into two tables *Table 1*: Low density polyethylene and *Table 2*: High density polyethylene. The critical density value for distinguishing between the two classifications was somewhat arbitrarily set at  $0.940 \text{ g cm}^{-3}$ . Therefore, *Table 1* contains data for Types I and II, (Edmunds, 1978), low and medium density polyethylene with many branched chains, while *Table 2* contains data for Types III and IV, (Edmunds, 1978) high density polyethylene with linear chains or few branches. The reason for this separation is so that comparisons may be made more easily among data for the same general type of polyolefin. For example, the more crystalline, high density polyethylenes generally yield lower values for the diffusion constant than do the less crystalline low density polyethylenes.

A letter following the number in the last column of annotated references refers to the polymer as identified in the annotated notes for cases in which values of several distinct samples are given in the same reference. Diffusion in polyolefins is affected by thermal history, mechanical treatment, solvent swelling, etc. Many of the references give quite different values for diffusion constants for specimens from the same polymer sample which have

undergone different pretreatment. Such facts are mentioned in the annotation, but the data for only one representative set of specimens are presented in the tables. Therefore, it is only when one reference includes data on two or more differing polymer samples of the same general category that a polymer identification letter is attached to the entry. This letter refers to the reference annotation description of the sample.

*Table 3* contains the data on diffusion in polyisobutylene. It has the same format as *Tables 1* and *2*.

The diffusion constants for polypropylene are listed in *Table 4*. As in the case of polyethylene, large differences in diffusion constants appear to result, at least in part, from differences in crystallinity; the highly crystalline isotactic samples have diffusion coefficients which average an order of ten lower than those of atactic polypropylene of low crystallinity. However, rather than setting up separate tables, a column was added to *Table 4* which gives the tacticity and calculated percentage crystallinity of each sample.

*Tables 5* and *6* contain diffusion data for hydrogenated polyisobutadiene and poly(4-methylpentene-1) respectively.

*Table 7* for ethylene-propylene copolymers includes a column for mole fraction propylene in the copolymers.

The final *Table 8* contains data on self diffusion for linear alkanes and for linear and branched polyolefins up to a molecular weight of about six thousand. Also, some diffusion constants for low molecular weight polyolefins (two to twenty-three thousand) in higher molecular weight polyisobutylene and polyethylene are repeated at the end of this Table.

#### ANNOTATED REFERENCES

This section contains data on the characterization of the polymers and migrants, a brief description of the method used to determine diffusion constants, and the

Table 2 High density polyethylene

Migrant	Mol. wt.	Type diffusion constant	Diffusion Constant* ( $10^{-8} \text{ cm}^2 \text{ s}^{-1}$ ) (Temperature range °C)	Log A	E (kJ mol <sup>-1</sup> )	Annot. ref.
Methane	16.0	$\bar{D}$	2.3 (10, 50)	0.38	43.5	1
Methane	16.0	$\bar{D}$	8.6 (25)	—	—	9a
Methane	16.0	$D$ (1 Atm)	1460 (140), 3800 (190)	—	—	34
Ethane	30.1	$\bar{D}$	0.51 (0, 50)	1.21	49.7	9a
Ethane	30.1	$\bar{D}$	0.51 (10, 50)	1.33	52.3	1
Ethane	30.1	$D_{C \rightarrow 0}$	1.80 (25)	—	—	35
Ethane	30.1	$\bar{D}$	1.08 (25, 50)	1.37	53.3	9b
Ethane	30.1	$\bar{D}$	2.4 (25, 50)	2.67	58.7	9c
Ethane	30.1	$\bar{D}$	0.87 (25, 50)	3.54	67.7	9d
Ethane	30.1	$\bar{D}$	2.3 (25, 60)	2.15	55.9	36a
Ethane	30.1	$\bar{D}$	1.43 (25, 60)	2.59	59.5	36b
Ethane	30.1	$D_{C \rightarrow 0}$	6.4 (40, 110)	0.55	46.4	37
Allene	40.1	$\bar{D}$	0.95 (10, 50)	0.68	47.3	1
Propylene	42.1	$\bar{D}$	0.37 (10, 50)	1.19	52.3	1
Cyclopropane	42.1	$D_{C \rightarrow 0}$	11.4 (70, 120)	1.81	57.5	37
Cyclopropane	42.1	$D_{C \rightarrow 0}$	1200 (140, 160)	-2.79	16.9	37
Propane	44.1	$\bar{D}$	0.156 (10, 50)	1.66	56.9	1
n-Butane	58.1	$\bar{D}$	0.36 (25)	—	—	9a
n-Butane	58.1	$D_{C \rightarrow 0}$	2.0 (40, 50)	2.70	62.3	37
n-Butane	58.1	$D_{C \rightarrow 0}$	900 (140, 160)	-2.65	19.0	37
n-Pentane	72.2	$\bar{D}$	0.33 (25, 50)	4.93	76.6	9a
2,2-Dimethylpropane	72.2	$\bar{D}$	0.31 (25, 50)	-2.17	36.2	9a
2,2-Dimethylpropane	72.2	$D_{C \rightarrow 0}$	0.58 (50, 80)	5.90	87.4	37
2,2-Dimethylpropane	72.2	$D_{C \rightarrow 0}$	470 (140, 160)	-1.93	26.9	37
Dichloromethane	84.9	$D_{C \rightarrow 0}$	2.7 (25, 60)	3.16	62.7	38
n-Hexane	86.2	$D_{C \rightarrow 0}$	75N4 (0)	—	—	11
Bromomethane	95.0	$D_{C \rightarrow 0}$	0.140 (0)	—	—	11
Trans-1,2-dichloroethylene	97.0	$\bar{D}_{C \rightarrow 0}$	38 (30)	—	—	39
Cis-1,2-dichloroethylene	97.0	$\bar{D}_{C \rightarrow 0}$	17.0 (30)	—	—	39
o-Xylene	106.2	$\bar{D}$	5.9 (30, 80)	0.73	46.2	39
o-Xylene	106.2	$\bar{D}$	10.0 (40)	—	—	40
p-Xylene	106.2	$\bar{D}$	13.8 (25, 70)	-1.21	32.2	20
p-Xylene	106.2	$\bar{D}$	11.1 (25, 70)	0.70	44.4	39
p-Xylene	106.2	$\bar{D}$	0.49 (25)	—	—	41
p-Xylene	106.2	$\bar{D}$	18.0 (40)	—	—	40
2,2,4-Trimethylpentane	114.2	$\bar{D}$	28.0 (50)	—	—	21a
2,2,4-Trimethylpentane	114.2	$\bar{D}$	37.0 (50)	—	—	21b
2,4-Dihydroxybenzophenone	214.2	$D_{C \rightarrow 0}$	0.23 (60, 70)	7.98	106.0	23
n-Octadecane	254.5	$D_{C \rightarrow 0}$	0.170 (30, 60)	5.82	84.6	63
n-Octadecane	254.5	$D_{g.c.}$	39 (150)	—	—	62
2-Hydroxy-4-methoxybenzophenone	228.2	$D_{C \rightarrow 0}$	0.52 (80, 110)	2.48	72.8	27
2-Hydroxy-4-butoxybenzophenone	270.3	$D_{C \rightarrow 0}$	0.30 (80, 110)	2.92	77.4	27
Dibutylphthalate	278.3	$DPVC$	<20N6 (70)	—	—	29
2-Hydroxy-4-octoxybenzophenone	326.4	$D_{C \rightarrow 0}$	0.0088 (50, 70)	14.98	155.0	31
2-Hydroxy-4-octoxybenzophenone	326.4	$D_{C \rightarrow 0}$	0.173 (80, 110)	4.60	90.4	27
Tricresyl phosphate	368.4	$DPVC$	<20N6 (70)	—	—	29
Dodecanyl dodecanate	368.6	$D_{C \rightarrow 0}$	290 (150)	—	—	26
2-Hydroxy-4-dodecoxybenzophenone	382.5	$D_{C \rightarrow 0}$	0.177 (80, 110)	1.64	70.3	27
Bis(2 ethylhexyl)phthalate	390.6	$DPVC$	16N4 (70)	—	—	29
2-Hydroxy-4-octadecoxybenzophenone	466.7	$D_{C \rightarrow 0}$	0.082 (80, 110)	1.43	71.1	27
Octadecyl octadecanate	537.0	$D_{C \rightarrow 0}$	170 (150)	—	—	26
Doconsanyl doconsanate	649.1	$D_{C \rightarrow 0}$	74 (130, 180)	-2.56	27.5	26

\* Diffusion constant calculated at lowest temperature of range. ( $aaNb = aa \times 10^{-b}$ )

assumptions made, equations utilized, and calculations performed to obtain the kinetic diffusion parameters in Tables 1 to 8 for each of the original references.

The justification for this lengthy section is twofold: (1) the large effects of structure and conditioning of the polymeric substrate on the diffusion process require as detailed a description as possible of the characterization and pretreatment of the polymers if the data in the tables are to be compared and their differences interpreted; (2) since diffusion constants for polymers are often a function of time, concentration and distance, a knowledge of the experimental conditions, methods of measurement and theoretical models evoked for the calculation of diffusion parameters are also essential for an understanding of the

data. The reference annotation is divided into four sections.

### Polymers

Due to the effects of physical and chemical properties and pretreatment of the polymeric substrates upon the diffusion parameters, as much information as was available in the source reference is presented. These include: names of manufacturers, trade names, batch designations, methods of polymerization, additives, processing and fabricating conditions, pretreatment, density, molecular weights, percentage crystallinity, branching, functional group content and any other

Table 3 Polyisobutylene

Migrant	Mol. wt.	Type diffusion coefficient	Diffusion Constant* ( $10^{-8}$ cm <sup>2</sup> s <sup>-1</sup> ) Temperature range (°C)	Log A	E (kJ mol <sup>-1</sup> )	Annot. ref.
Propane	41.2	$\bar{D}_{C \rightarrow 0}$	0.30 (30)	—	—	42
n-Butane	58.1	$\bar{D}_{C \rightarrow 0}$	0.122 (25, 40)	3.60	71.5	43
Isobutane	58.1	$\bar{D}_{C \rightarrow 0}$	0.045 (23, 40)	3.88	75.0	43
n-Pentane	72.2	$\bar{D}_{C \rightarrow 0}$	0.107 (25, 40)	3.20	69.5	43
n-Pentane	72.2	$\bar{D}_{C \rightarrow 0}$	0.120 (25, 60)	3.32	69.9	44
2-Methylbutane	72.2	$D_{C \rightarrow 0}$	0.048 (25, 40)	4.39	78.2	43
2-Methylbutane	72.2	$D_{C \rightarrow 0}^*$	0.152 (30)	—	—	51
2,2-Dimethyl propane	72.2	$\bar{D}_{C \rightarrow 0}$	0.022 (25, 40)	2.74	70.7	43
Benzene	78.1	$D_{C \rightarrow 0}$	77 (70)	—	—	45
Cyclohexane	84.2	$\bar{D}_{C \rightarrow 0}$	0.177 (40, 60)	1.95	64.2	44
Methylcyclopentane	84.2	$\bar{D}_{C \rightarrow 0}$	0.097 (30)	—	—	44
n-Hexane	86.2	$\bar{D}_{C \rightarrow 0}$	0.195 (30)	—	—	44
2-Methyl pentane	86.2	$\bar{D}_{C \rightarrow 0}$	0.117 (30)	—	—	44
3-Methyl pentane	86.2	$\bar{D}_{C \rightarrow 0}$	0.104 (30)	—	—	44
Methyl cyclohexane	98.2	$D_{C \rightarrow 0}$	0.088 (30)	—	—	44
n-Heptane	100.2	$D_{C \rightarrow 0}$	0.195 (30)	—	—	44
n-Octane	114.2	$D_{C \rightarrow 0}$	0.117 (25, 40)	4.37	75.9	44
n-Octane	114.2	$D_V$	1650 (100)	—	—	25
2,2,5-Trimethyl pentane	128.3	$\bar{D}_{C \rightarrow 0}$	0.040 (25, 50)	3.17	71.2	44
n-Dodecane	168.3	$D_{C \rightarrow 0}$	0.0176 (20, 25)	3.34	71.2	46
n-Dodecane	168.3	$D_V$	600 (100)	—	—	25
1,1-Diphenylethane	182.3	$D_{C \rightarrow 0}$	0.033 (25, 50)	3.49	74.1	47
1,1,2-Trichloroethane	187.4	$D_{C \rightarrow 0}$	3.0 (25)	—	—	48
Phenyl-2-naphthalene	219.3	$D_{C \rightarrow 0}$	2.2 (70, 90)	1.40	59.6	49
n-Hexadecane	226.4	$D_{C \rightarrow 0}$	0.034 (20, 40)	2.62	67.9	46
n-Hexadecane	226.4	$D_{C \rightarrow 0}$	0.106 (25, 50)	3.92	73.6	50
n-Hexadecane	226.4	$D_V$	250 (90, 110)	3.01	61.5	25
n-Octadecane	254.5	$D_{C \rightarrow 0}$	9.7 (100, 120)	1.00	49.9	28a
n-Octadecane	254.5	$D_{C \rightarrow 0}$	19.7 (100, 120)	-4.81	13.5	28b
Octadecanol	270.5	$D_{C \rightarrow 0}$	15.6 (100, 120)	-0.75	43.3	28b
Paraffin	~325	$D_{V \rightarrow 0}$	0.74 (60, 100)	3.79	76.0	30
Paraffin	~325	$D_V$	85 (100, 120)	0.74	48.7	25
Ceresin	~450	$D_{V \rightarrow 0}$	15.8 (120, 130)	1.26	60.7	33
Ceresin	~525	$D_{V \rightarrow 0}$	6.9 (100)	—	—	25
Ceresin	~525	$D_V$	18.8 (100, 120)	1.30	57.3	25
Octadecyloctadecanoate	537.0	$D_{C \rightarrow 0}$	4.6 (100, 120)	-1.33	43.0	28b
Octadecanoic acid (dimer)	597.0	$D_{C \rightarrow 0}$	7.4 (100, 120)	-2.86	30.5	28b
Ceresin	~600	$D_{V \rightarrow 0}$	6.6 (100, 120)	-1.33	41.8	33
Polyethylene	~2000	$D_V$	0.24 (100, 120)	1.82	74.0	25
Polyethylene	~2000	$D_{V \rightarrow 0}$	0.39 (100, 120)	—	—	25
Polyethylene	~5000	$D_{V \rightarrow 0}$	0.060 (130)	—	—	25

\* Diffusion constants calculated at lowest temperature of range

information which might aid in the characterization of the polymers.

#### Migrants

The sources, pretreatment and stated purity of the migrant materials are given. No data were available in about forty per cent of the references. Actually, these data on the properties of the migrants are probably of marginal usefulness in most cases.

#### Method

A short summary is given of the experimental methods used, physical properties measured and special techniques which were employed. This information is important for two reasons: (1) the type of diffusion constant which is measured depends on the experimental method which is used; (2) a knowledge of the method is necessary as background for understanding the discussion in the subsequent section on mathematical models and calculations.

#### Calculation

The sections on calculation include (1) assumptions made in the formulation of the mathematical model; (2)

the sections and equations by Crank (1975) in which the model and methods are discussed in more detail; (3) the type of calculations made; (4) the source in the reference from which the data were taken, and (5) the means by which the data were transformed into the entries in the tables.

In this section, any apparent errors, inconsistencies, or lack of correspondence in the presented data are pointed out. Also, the models and methods used to extrapolate diffusion constants to zero concentration, pressure or fractional volume of migrant are indicated and, in some cases, the values of the parameters of the equations used for the extrapolation procedure are listed.

#### Notes

Notes have been appended to the annotation in a number of cases to alert the reader to extra information and experiments of interest in the source reference. These include information on the effects of annealing, stretching, cold drawing, solvent swelling, oxidation, and  $\gamma$ -ray irradiation and grafting upon the diffusion process. These notes also include information on the effects of molecular weight, specimen thickness, surface layer, etc., on diffusion constants. The availability in the source reference of

Table 4 Polypropylene

Migrant	Mol. wt.	Type diffusion coefficient	Tact <sup>a</sup> (%CR.)	Diffusion constant (10 <sup>-8</sup> cm <sup>2</sup> s <sup>-1</sup> ) (Temperature range °C)	Log A	E (kJ mol <sup>-1</sup> )	Annot. ref.
Benzene	78.1	D <sub>C→0</sub>	AT (10)	0.17 (10, 40)	6.55	83.3	52
Chlorofluoromethane	86.5	D (1 Atm)	—	4200 (190)	—	—	17
Tetrafluoromethane	88.0	$\bar{D}$	IS (95)	1.11 (40, 70)	2.61	66.3	61
Toluene	91.1	D <sub>C→0</sub>	IS (74)	0.0179 (0, 50)	1.26	57.6	53
Toluene	91.1	$\bar{D}$	IS (65)	37.0 (40)	—	—	40
Methylcyclohexane	98.2	D <sub>C→0</sub>	IS (74)	0.00126 (0, 50)	3.68	76.3	53
Methylcyclohexane	98.2	$\bar{D}$	IS (65)	11.0 (40)	—	—	40
n-Heptane	100.2	D <sub>C→0</sub>	IS (74)	0.0027 (0, 50)	3.84	75.3	53
p-Xylene	106.2	$\bar{D}$	IS (65)	28.0 (40)	—	—	40
o-Xylene	106.2	$\bar{D}$	IS (65)	14.0 (40)	—	—	40
2,2,4-Trimethylpentane	114.2	$\bar{D}$	IS (65)	5.0 (40)	—	—	40
Phenylthiozine	199.3	D <sub>C→0</sub>	IS —	0.23 (80, 110)	11.49	136.1	54
Dimethyl-3,3'-thiodipropionate	206.3	D <sub>C→0</sub>	— (16)	0.140 (20, 30)	5.38	79.9	27
Dimethyl-3,3'-thiodipropionate	206.3	D <sub>C→0</sub>	IS (63)	0.76 (80, 110)	2.46	71.5	55
2,4-Dihydroxybenzophenone	214.2	D <sub>C→0</sub>	IS (65)	0.0072 (40, 70)	6.22	98.0	23
2,5-Ditertbutyl-4-hydroxytoluene	220.3	D <sub>C→0</sub>	IS —	0.34 (60, 110)	6.31	94.3	54
2-Hydroxy-4-methoxybenzophenone	228.2	D <sub>C→0</sub>	ST (24)	2.4 (70, 90)	0.08	50.6	27
2-Hydroxy-4-methoxybenzophenone	228.2	D <sub>C→0</sub>	IS (63)	0.37 (80, 110)	2.83	76.1	55
2-Hydroxy-4-butoxybenzophenone	270.3	D <sub>C→0</sub>	ST (24)	1.24 (70, 90)	1.58	62.3	27
2-Hydroxy-4-butoxybenzophenone	270.3	D <sub>C→0</sub>	IS (63)	0.24 (80, 110)	3.45	81.6	55
Dibutylphthalate	278.3	DPVC	—	51N4 (80)	—	—	29
Paraffin	~325.0	D <sub>V→0</sub>	AT —	17.2 (60, 90)	-1.39	34.3	30
Paraffin	~325.0	D <sub>V</sub>	AT —	250 (110, 120)	3.00	63.1	25
2-Hydroxy-4-octoxybenzophenone	326.4	D <sub>C→0</sub>	ST (24)	1.37 (70, 90)	2.77	69.9	27
2-Hydroxy-4-octoxybenzophenone	326.4	D <sub>C→0</sub>	IS (63)	1.35 (80, 110)	4.00	87.0	55
Dihexyl 3,3'-thiodipropionate	346.5	D <sub>C→0</sub>	— (16)	0.087 (20, 30)	5.26	80.3	27
Dihexyl 3,3'-thiodipropionate	346.5	D <sub>C→0</sub>	IS (63)	0.35 (80, 110)	3.05	77.8	55
n-Octadecyldietanolamine	357.6	D <sub>C→0</sub>	IS (60)	0.82 (80, 130)	4.60	85.8	32
Tricresylphosphate	368.4	DPVC	—	<20N6 (70)	—	—	29
2-Hydroxy-4-dodecoxybenzophenone	382.5	D <sub>C→0</sub>	ST (24)	2.2 (70, 90)	5.07	83.7	27
2-Hydroxy-4-dodecoxybenzophenone	382.5	D <sub>C→0</sub>	IS (63)	0.101 (80, 110)	4.18	89.1	55
Bis(2-ethylhexyl)phthalate	390.6	DPVC	—	13N5 (40, 70)	2.39	85.6	29
Ceresin	~450	D <sub>V→0</sub>	AT —	71 (120, 130)	-0.103	45.5	33
2-Hydroxy-4-octadecyloxybenzophenone	466.7	D <sub>C→0</sub>	ST (24)	0.67 (70, 90)	3.41	76.1	27
2-Hydroxy-4-octadecyloxybenzophenone	466.7	D <sub>C→0</sub>	IS (63)	0.068 (80, 110)	5.49	99.2	55
Didodecyl-3,3'-thiodipropionate	514.8	D <sub>C→0</sub>	IS (60)	0.082 (80, 150)	3.90	82.8	32
Didodecyl-3,3'-thiodipropionate	514.8	D <sub>C→0</sub>	IS (63)	0.157 (80, 110)	3.76	84.9	55
Ceresin	~525	D <sub>V</sub>	AT —	81 (110, 120)	2.50	63.1	25
1,1,3-Tri[2-methyl-4-hydroxy-5-(t-butyl)phenyl]butane	544.8	D <sub>C→0</sub>	IS (60)	0.138 (100, 150)	4.20	93.3	32
Ceresin	~600	D <sub>V→0</sub>	AT —	32 (100, 120)	-1.55	35.3	33
Dihexadecyl, 3,3'-thiodipropionate	627.0	D <sub>C→0</sub>	IS (63)	0.096 (80, 110)	4.28	89.9	55
Polyethylene	~2000	D <sub>V</sub>	AT —	5.6 (100, 110)	5.42	93.0	25

<sup>a</sup> IS, isotactic; ST, stereoblock; AT, atactic\* Diffusion constant calculated at lowest temperature of range ( $aa/Nb = aa \times 10^{-b}$ )

Table 5 Hydrogenated polybutadiene

Migrant	Mol. wt.	Type diffusion coefficient	Constant* (10 <sup>-8</sup> cm <sup>2</sup> s <sup>-1</sup> ) (Temperature range °C)	Log A	E (kJ mol <sup>-1</sup> )	Annot. ref.
Methane	16.0	$\bar{D}$	22 (10, 50)	1.43	43.9	1
Ethane	30.1	$\bar{D}$	8.9 (10, 50)	2.03	49.4	1
Allene	40.1	$\bar{D}$	12.5 (10, 50)	1.41	45.2	1
Propylene	42.1	$\bar{D}$	7.6 (10, 50)	1.73	48.1	1
Propane	44.1	$\bar{D}$	4.2 (10, 50)	2.24	52.3	1
n-Octadecane	254.5	D <sub>C→0</sub>	8.0 (40, 60)	0.57	46.0	27

\* Diffusion constant calculated for lowest temperature of range

diffusion constants at other concentrations and pressures of migrant and from other measurement techniques are also noted.

## DISCUSSION

It is clear from the preceding data presentation that it would be futile, either by weighted average or critical

judgment, to evolve 'best values' or 'percentage error' for the data in Tables 1 through 8. However, one can indicate some of the trends which are easily noted in the data and discuss qualitatively the nature of some of the perturbing factors which bring about large variation in diffusion parameters for what appear otherwise to be identical polymer-migrant systems. The discussion will follow the same format as the annotated references, viz., Polymers, Migrants, Methods, and Calculations.

Table 6 Poly(4-methylpentene-1)

Migrant	Mol. wt.	Type Diffusion coefficient	Diffusion constant* ( $10^{-8} \text{ cm}^2 \text{ s}^{-1}$ ) (Temperature range °C)	Log A	E (kJ mol <sup>-1</sup> )	Annot. ref.
Didodecyl-3,3'-thiodipropionate	514.8	$D_{C \rightarrow 0}$	4.1 (150, 200)	0.10	60.7	32
1,1,3-Tri[2-methyl-4-hydroxy-5 (t-butyl)phenyl]butane	544.8	$D_{C \rightarrow 0}$	0.24 (140, 200)	-1.10	59.4	32

Table 7 Ethylene-propylene copolymers

Migrant	Mol. wt.	Fraction propylene	Type diffusion constant	Diffusion constant* ( $10^{-8} \text{ cm}^2 \text{ s}^{-1}$ ) (Temperature range °C)	Log A	E (kJ mol <sup>-1</sup> )	Annot. ref.
n-Pentane	72.2	0.51	$D_{C \rightarrow 0}$	7.0 (25)	—	—	52
Benzene	78.1	0.31	$D_{C \rightarrow 0}$	4.8 (10, 40)	0.71	43.6	52
Benzene	78.1	0.51	$D_{C \rightarrow 0}$	2.2 (10, 40)	2.44	54.9	52
Benzene	78.1	0.72	$D_{C \rightarrow 0}$	0.78 (10, 40)	3.48	63.0	52
Cyclohexane	84.2	0.51	$D_{C \rightarrow 0}$	2.5 (25)	—	—	52
Methylchloride	84.9	0.51	$D_{C \rightarrow 0}$	15.3 (25)	—	—	52
n-Hexane	86.2	0.51	$D_{C \rightarrow 0}$	4.9 (25)	—	—	52
2,4-Dihydroxybenzophenone	214.2	0.03**	$D_{C \rightarrow 0}$	0.036 (40, 70)	7.09	99.2	23
2-Hydroxy-4-octoxybenzophenone	326.4	0.03**	$D_{C \rightarrow 0}$	0.0143 (50, 70)	14.91	153	31

\* Diffusion constant calculated for lowest temperature of range

\*\* HDPE

Table 8 Self diffusion of polyolefins

Substances (s) (Mol. wt.)	Method <sup>a</sup>	Type diffusion constant	Diffusion constant ( $10^{-8} \text{ cm}^2 \text{ s}^{-1}$ ) (temperature range °C)	Log A	E (kJ mol <sup>-1</sup> )	Annot. ref.
n-Pentane (72.2)	RA	D*	1265 (-80, 40)	-3.09	6.68	56
n-Pentane (72.2)	SE	D	1070 (-90, 40)	-3.13	6.44	57
n-Hexane (86.2)	SE	D	470 (-90, 60)	-2.86	8.66	57
n-Heptane (100.2)	RA	D*	388 (-80, 100)	-2.87	9.40	56
n-Heptane (100.2)	SE	D	306 (-90, 120)	-2.90	9.16	57
n-Octane (114.2)	SE	D	641 (-40, 70)	-2.93	10.1	57
n-Nonane (128.3)	SE	D	399 (-40, 80)	-2.51	12.9	57
n-Decane (142.3)	SE	D	337 (-30, 80)	-2.27	14.9	57
n-Octadecane (254.5)	SE	D	378 (40, 160)	-2.67	16.5	57
Paraffin (~325)	INT	D	210 (60, 90)	-1.92	24.0	30
n-Dotriacontane (450.9)	SE	D	195 (80, 160)	-2.22	23.6	57
Polyisobutylene (~700)	SE	D	38 (110, 180)	-3.34	22.6	58
High density polyethylene (~4100)	SE	D	12.2 (130, 190)	-4.04	22.2	59
High density polyethylene (~5800)	SE	D	10.2 (140, 190)	-4.91	16.4	59
Polyethylene (~2000) in-polyisobutylene	INT	$D_{V \rightarrow 0}$	39 (100)	—	—	25
High density polyethylene (3600) in low density polyethylene ( $1 \times 10^5$ )	i.r.	$D_{C \rightarrow 0}$	3.0 (180)	—	—	26
HDPE (4600) in LDPE ( $1 \times 10^5$ )	i.r.	$D_{C \rightarrow 0}$	1.86 (180)	—	—	26
Polyethylene (~5000) in polyisobutylene	INT	$D_{V \rightarrow 0}$	0.060 (130)	—	—	25
HDPE (11 000) in LDPE ( $1 \times 10^5$ )	i.r.	$D_{C \rightarrow 0}$	0.34 (180)	—	—	26
HDPE (17 000) in LDPE ( $1 \times 10^5$ )	i.r.	$D_{C \rightarrow 0}$	0.150 (180)	—	—	26
HDPE (23 000) in LDPE ( $1 \times 10^5$ )	i.r.	$D_{C \rightarrow 0}$	0.081 (180)	—	—	26

<sup>a</sup> RA: radioactive migrant; SE: spin-echo; INT: interference micromethod; i.r.: infra-red

### Polymers

A rough comparison in the tables of the polymer substrates for the same migrants justifies the division of the tables into separate polymer classifications. The values for the diffusion constants for LDPE are fairly consistently about four times as large as those for HDPE for the same migrants and temperature range. A similar comparison between LDPE and polyisobutylene demonstrates somewhat more erratic behaviour; the diffusion constants in LDPE range from five to two

hundred times the size of those for comparable migrants in polyisobutylene. On the other hand, diffusion constants in hydrogenated polybutadiene average about three times greater than those in LDPE. The polypropylene data exhibit much less consistency; diffusion is sometimes slower, sometimes faster than in LDPE. Of course, much of this variation here can be attributed qualitatively to differences in tacticity (and therefore in percentage crystallinity) in the polypropylene specimens.

The activation energies for both LDPE and HDPE,



below their melting points, average about 13 kcal mol<sup>-1</sup>. The more slowly diffusing polypropylenes and polyisobutylenes yield *E* values averaging around 20 and 17 kcal mol<sup>-1</sup>, respectively, while more rapidly diffusing hydrogenated butadienes give an average *E* of about 11 kcal mol<sup>-1</sup>. Since few experiments cover temperature ranges of greater than 30°–40°C, many of the differences in *E* and log *A* values in the tables may be due to experimental errors, either random or systematic.

A comparison of diffusion constants of both LDPE and HDPE below and above their melting points shows a discontinuity in the melting region. (The inverse gas chromatography data were excluded from this analysis for reasons to be discussed subsequently.) The increase in diffusion constant is greater than that naively expected for an increase in the amorphous content to 100%. (Crystalline regions are generally assumed to contribute negligibly to the diffusion process.) The activation energy for diffusion falls to values of about 6 kcal mol<sup>-1</sup> at temperatures above the melting point.

The values for *E* of self diffusion coefficients in Table 8 increase in a regular manner as they progress to longer chain lengths. The value for the energy of activation for self diffusion levels off to a value of a little less than six kcal mol<sup>-1</sup> at chain lengths of greater than 25–30 methylene units. Some of the consistency of these results may reflect the fact that they are mainly from a single method and apparatus. The comparatively lower diffusion coefficients for the low molecular–high molecular weight systems at the bottom of Table 8 may be due to the branched character of the migrants.

The annotated references summarize much diffusion rate data for the effects of various treatments on and modifications of the polymer substrates. The causes for many of these effects and differences in diffusion rates lie in the morphological and geometrical patterns formed in the polymer matrix by the treatments (e.g., pores, channels, etc.). Further discussion of these effects can be found in many of the original references.

### Migrants

The rates of diffusion for the polymer substrates in each of the eight tables show a decidedly decreasing trend with increasing molecular weight of the migrant. Comparison of migrants with similar molecular weights indicate that other obvious factors such as the molecular cross section of the migrant and polymer–migrant interactions have strong influences on the diffusion rates.

Unsurprisingly, both polar groups and chain branching in migrants considerably decrease their rate of diffusion in polyolefins. However, halogenated molecules and molecules containing aromatic rings diffuse much more rapidly than do aliphatic migrants of comparable molecular weight.

### Methods

The three principle methods used to determine the diffusion coefficients listed in these tables, permeation, sorption–desorption, and concentration gradient measurements, give reasonably comparable values especially when the differences in type of diffusion constants measured by them are taken into consideration (e.g., some measure concentration average and others initial, final, intermediate, or extrapolated values for the

diffusion constant). The agreement is, in fact, better than one might expect.

However, the diffusion constants from two of the methods are given special designations. The reasons for this are not only because their values are out of line with those from other methods, but also because there are other considerations which tend to confirm that they do not correctly represent the diffusion process.

The first of these special symbols, *D*<sub>PVC</sub>, refers to the diffusion constants calculated from the work by Thinius (1964) in which diffusion was measured into a polymer sheet from a contiguous sheet of poly(vinyl chloride) containing 35% by weight of migrant. Diffusion through a laminate (Crank, p260f) can lead to complications at the interface. The values for *D*<sub>PVC</sub> are several powers of ten slower than diffusion constants for comparable cases from other methods.

The diffusion constants obtained from inverse gas chromatography are also given a special designation, *D*<sub>g.c.</sub>. Again, these data do not correlate well with those from the other methods. They do not show a discontinuity at the polymer melting point, nor a smaller temperature coefficient above the melting point. Also, there is great inherent uncertainty in the thickness of the polymer layer and, in this technique, the thickness enters as a squared term in the calculation of *D*<sub>g.c.</sub>.

The significances in the differences in other types of diffusion constants are discussed in the section immediately following.

### Calculation

Fick's first law,  $F = -D\partial C/\partial x$ , as defined in equation (1), may be used directly to determine *D* for the case of steady state diffusion where the diffusion constant is independent of concentration, thus

$$F = D(C_1 - C_2)l^{-1} \quad (3)$$

where *F* is the flux or rate of transfer across the boundary of a film of thickness, *l*, and *C*<sub>1</sub> and *C*<sub>2</sub> are the concentrations of migrant on either side. Likewise, if there is steady state permeation of a gaseous migrant through a polymer film placed across a pressure gradient, Δ*p*, then

$$F = P\Delta pl^{-1} \quad (4)$$

where *P* is the permeation coefficient. If the diffusion coefficient is constant and the sorption isotherm is linear (i.e., obeys Henry's law), then *D* may be calculated from

$$D = PS^{-1} \quad (5)$$

where *S* is the equilibrium solubility.

In some of the data sources for this paper where steady state diffusion is a reasonable assumption, equations (3) or (4) and (5) have been used to calculate diffusion coefficients. However, if nonsteady state diffusion is being measured and, as seems to be the case in most migrant–polymer systems reviewed here, the diffusion constant is concentration dependent, then Fick's second law

$$\frac{\partial C}{\partial t} = \text{div}(D \text{ grad } C) \quad (6)$$

is either solved or fitted at reasonable boundary

conditions dictated by the experiment.

In each annotated reference in the section on calculations, reference is made to the appropriate sections of Crank (1975) in which the solution to equation (6) used in the reference of interest is developed and discussed.

As a result of differing experimental techniques, boundary conditions and concentration (or partial volume) dependence of the diffusion constant, a number of differently defined diffusion constants have evolved and many of these were listed and briefly defined near the beginning of Section III. Without becoming involved herein with the ramifications of these definitions (which are discussed in detail in Chapter 10 of Crank (1975)), we will make a few comparisons from the data in the tables as to the relative size and the concentration dependence of the various diffusion coefficients as applied to the measurement of diffusion of organic migrants in polyolefins.

The most frequently occurring type of diffusion coefficient in the eight tables is  $D_{c \rightarrow 0}$  which is found in over a hundred listings. Along with  $\bar{D}_{c \rightarrow 0}$ ,  $D_{V \rightarrow 0}$  and  $D_{c \rightarrow 0}^*$ , it refers to 'extrapolation' of the respective diffusion coefficient to zero concentration or volume fraction of migrant. Although such extrapolations were performed in some cases, especially in the case of  $\bar{D}_{c \rightarrow 0}$ , which is discussed below, in many other cases it merely symbolizes the fact that statements were made to the effect that the concentration of the migrant was low enough for concentration effects to be ignored, or that the diffusion constant was found to be independent of concentration in the range of investigation. This rationalization was most prevalent in the cases of higher molecular weight migrants where their concentrations were generally less than 5%.

Concentration average diffusion constants,  $\bar{D}$ , were obtained in the main in investigations of diffusion of lower molecular weight migrants.  $\bar{D}$  is usually defined by equation (7)

$$\bar{D} = C_0^{-1} \int_0^{C_0} D dC \quad (7)$$

where the concentration range is 0 to  $C_0$ . An approximate  $\bar{D}$  is assumed to be obtained from time-lag permeation-type methods.  $\bar{D}$  is approximated in sorption-desorption experiments by  $1/2(\bar{D}_s - \bar{D}_d)$ , where  $\bar{D}_s$  and  $\bar{D}_d$  are obtained from the half-times of adsorption and desorption respectively.

In most of the cases in which the average diffusion coefficient,  $\bar{D}$ , was extrapolated to zero concentration, the relationship in Equation (8)

$$\bar{D}_{c \rightarrow 0} = \bar{D} \exp(-\gamma C) \quad (8)$$

was used to obtain  $\bar{D}_{c \rightarrow 0}$ .

In cases where comparable data exist, values of diffusion coefficients extrapolated to zero, viz.,  $D_{c \rightarrow 0}$ ,  $\bar{D}_{c \rightarrow 0}$ ,  $D_{V \rightarrow 0}$ ,  $D_{V \rightarrow 0}^*$  and  $D_{c \rightarrow 0}^*$ , are considerably lower than the respective higher concentration values from which they were extrapolated, i.e.,  $\gamma > 0$  in equation (8). If  $\gamma$  is measured in (g/g), its values range from unity to several hundred and increase with temperature. The parameter,  $\gamma$ , also appears to increase with increasing molecular weight of the migrant, but the data suggesting this is taken from several experimental methods and obtained by several

techniques, so it is somewhat indecisive. In a similar manner, for cases in which the migrants are in the gaseous state, diffusion constants increase with pressure in all cases documented in this paper.

In a similar manner to the case of  $\bar{D}$ , the mutual diffusion coefficient,  $D^V$ , (see p. 205 Crank (1975)), is considerably larger than the intrinsic diffusion coefficient extrapolated to zero volume fraction migrant,  $D_{V \rightarrow 0}$ , from comparable cases. The two coefficients are related by the equation:  $D = D^V(1 - V)^{-1}$ .

A final observation which is quite striking is the extraordinarily good linear relationships which can be obtained from each of the tables by a plot of  $\log A$  vs.  $E/2.3 RT$  for all of the entries. This does not come as a surprise as the same effect has been shown for the diffusion of gases in elastomers by Barrer (1942), van Amerongen (1946) and Barrer (1948). It is also found for viscous flow and in cases in which the Arrhenius equation is applied to many other condensed phases processes. The explanation for this phenomenon, in terms of the transition state model, would appear to be that, for each polymer matrix, the free energy change (or equilibrium constant) for the activated state is invariant and independent of migrant or other factors affecting the rate of diffusion. However, from a more prosaic point of view, the effect may be an indication of the uncertainty of the temperature coefficient when determined through a narrow window of diffusion rates and over a short temperature range. Thus errors in calculated value of  $E$  would be compensated for by a corresponding change in  $\log A$ .

In conclusion, the comparability and consistency in these tables are indeed remarkable if one considers the great variation in diffusion coefficients for the same migrant-polymer pair which can be brought about by thermal, mechanical or solvent action, and the diverse methods of measurement and data treatment.

## KEY TO ANNOTATED REFERENCES

Trade names and names of commercial suppliers are identified in this section to aid in the characterization of materials. This does not imply endorsement by the National Bureau of Standards nor that they are necessarily the best available for the purpose.

HDPE	High density polyethylene
LDPE	Low density polyethylene
HPBD	Hydrogenated polybutadiene
PP	Polypropylene
PIB	Polyisobutylene
PMP	Poly (4-methylpentene-1)
$\rho$	Density ( $\text{g cm}^{-3}$ )
$M_1$	Number average molecular weight
$M_2$	Weight average molecular weight
$M_v$	Viscosity average molecular weight
$M$	Molecular weight
CH <sub>3</sub>	Methyl groups per 1000 Carbon Atoms
CO	Carboxyl groups per 1000 Carbon Atoms
C=C	Double bonds per 1000 Carbon Atoms
%	Percentage crystallinity (polymer), or percentage purity (migrant)
$l$	Film thickness (mm)
VIS	Viscosity
MP	Melting point
MI	Melt flow index

$\gamma$  Exponential concentration coefficient (g/g) in  $D = D_{c \rightarrow 0} \exp(\gamma C)$ .

## ANNOTATION REFERENCES

## (1) Michaels (1961)

*Polymers.* HDPE: 'GreX' from W. R. Grace by the Phillips process;  $CH_3$ , 1.5;  $M_1$ , 40 000;  $\rho$ , 0.964; 77%. LDPE: Alathon 14 from DuPont by high pressure process;  $CH_3$ , 30;  $M_1$ , 26 000;  $\rho$ , 0.914; 43%. HPBD: Hydropol, Phillips, hydrogenated in emulsion at 5°C;  $CH_3$ , 52; C=C, 13;  $M_1$ , 100 000;  $\rho$ , 0.894; 29%.

*Migrants.* Methane, >99%; ethane, >95%; allene, >95%; propylene, >99%; propane, >99%. Obtained from commercial suppliers and dried over calcium sulphate.

*Method.* Time lag permeation; pressure increase measured manometrically.

*Calculation.* Concentration independent diffusion constants were calculated by the time lag method (Crank, p 51). Data were calculated from  $\bar{D}$  at 25°C in Table 2 and  $E$  from Table 3.

## (2) Kanitz (1970)

*Polymers.* LDPE: from Canadian Industries Ltd.; no plasticizer or antiblock agents;  $\rho$ , 0.916; 54%;  $MI$ , 7.0 g/10 min.

*Migrant.* Methane, Matheson of Canada, high purity.

*Method.* Non steady state time-lag permeation, pressure of evacuated side measured.

*Calculation.* Concentration independent diffusion constants were calculated by the non-steady state time-lag method (Crank, p 51).  $\bar{D}$  data were calculated from the Arrhenius parameters in Table 1 where  $D_0$  should read  $\ln D_0$ .

*Notes.*  $\bar{D}$  for methane in LDPE increased upon  $\gamma$ -irradiation in both air and vacuum. LDPE density increased and crystallinity decreased upon  $\gamma$ -irradiation.

## (3) Li (1964)

*Polymer.* LDPE:  $\rho$ , 0.922; 47%;  $l$ , 0.004–0.016.

*Migrants.* Methane, no data.

*Method.* Steady state permeation measured volumetrically with mercury slug capillary. Solubility constants are from other references.

*Calculation.*  $\bar{D}$  (1 atm) calculated from (permeability) (solubility)<sup>-1</sup>. Data extrapolated from 33° to 30°C assuming  $E = 13 \text{ kcal mol}^{-1}$ .

## (4) Rosolovskaya (1976)

*Polymer.* LDPE:  $\rho$ , 0.927.

*Migrants.* Methane, benzene, carbontetrachloride, no data.

*Method.* Inverse gas chromatography, column packed with 60 mesh glass beads coated with polymer, 0.7 to  $2.9 \times 10^{-4}$  cm thick.

*Calculation.* VanDeemeter equation with  $8/\pi^2$  replaced by  $2/3$ . Data approximated—see note.

*Notes.*  $D$  values increased 3–10 fold over the polymer film thickness range, 0.7 to  $2.9 \times 10^{-4}$  cm, and exhibited inconsistencies.

## (5) Lundberg (1962)

*Polymer.* LDPE: high pressure;  $\rho$ , 0.921; 52%.

*Migrant.* Methane, Matheson, C.p.,  $\geq 99\%$ .

*Method.* Sorption measured monometrically up to 650 atm. for liquid polymer constrained to a cylindrical shape in a pressure vessel.

*Calculation.* Concentration independent diffusion constants were calculated for a stirred solution in a cylinder (Crank, pp 77–78); pressures were corrected for compressibility factor and  $D$  values extrapolated to one atmosphere. Data were obtained from a linear extrapolation of values in Table 2 of Lundberg (1964).

## (6) Tock (1976)

*Polymer.* LDPE: no data.

*Migrant.* Formaldehyde; from a mixture.

*Method.* Inverse gas chromatography; column packed with powdered polymer; particle size not given.

*Calculation.* Equation for non-steady state diffusion into a sphere (Crank p 91) for constant surface concentration is reduced to an equation for initial rate of vapour uptake. The latter equation is combined with an equation for equilibrium gas chromatography.

## (7) Evnochides (1971)

*Polymer.* LDPE: from Monsonoto (MPE 72) moulded at 160°C;  $M_1$ , 14 000;  $M_2$ , 351 000;  $\rho$ , 0.918; 48%;  $MI$ , 6.1.

*Migrant.* Ethane, CP grade, Matheson, 99.3% (0.5% Hydrogen, 0.1% methane, 0.1% ethylene).

*Method.* Sorption determined gravimetrically.

*Calculation.* Diffusion from a constant surface concentration into an infinite sheet (Crank p 48); Initial rates used to calculate  $D$  (Crank p 244).  $D$  values extrapolated to zero concentration. Data for  $D_{c \rightarrow 0}$ ,  $E$  and  $\gamma$  obtained from Figure 6;  $\gamma = 1.05$  (–30°C), 88 (30°C) (g/g).

## (8) Envochides (1970)

*Polymer.* LDPE: see (7) Evnochides (1971).

*Migrant.* Ethane, see (7) Evnochides (1971).

*Method.* Gravimetric sorption and desorption measured by phase lag and amplitude change for low frequency sinusoidal pressure variation.

*Calculation.* Concentration independent diffusion into both sides of an infinite sheet with surface equilibrium was assumed. (Crank p 217). Data for  $E$  and  $D$  calculated from values in Table 1 for 2.88 atm. pressure.

## (9) Brandt (1959)

*Polymer.* HDPE (a):  $\rho$ , 0.951;  $CH_3$ , 2;  $M_2$ , 140 000;  $l$ , 0.004–0.016. HDPE (b):  $\rho$ , 0.964;  $CH_3$ , 3;  $M_2$ , 78 000;  $l$ , 0.004–0.016. HDPE (c):  $\rho$ , 0.951,  $CH_3$ , 5,  $M_2$ , 575 000;  $l$ , 0.004–0.016. HDPE (d):  $\rho$ , 0.964;  $CH_3$ , 14;  $M_2$ , ~20 000;  $l$ , 0.004–0.016. LDPE (a):  $\rho$ , 0.918;  $CH_3$ , 25;  $M_2$ , 300 000;  $l$ , 0.004–0.016. LDPE (b):  $\rho$ , 0.910;  $CH_3$ , 33;  $M_2$ , 510 000;  $l$ , 0.004–0.016.

*Migrants.* Methane, ethane, propane, n-butane, n-pentane, 2,2'-dimethyl propane, no data.

*Method.* Time lag permeation, measured monometrically.

*Calculation.* Non-steady state diffusion into an infinite sheet (Crank, eq. 4.24a) fitted by successive approximations.

(10) Yasuda (1964)

*Polymers.* LDPE:  $\rho$ , 0.916;  $l$ , 0.025; 'blown'.

*Migrants.* Ethane, >99.5%.

*Method.* Time lag permeation measured monometrically.

*Calculations.* Concentration independent diffusion constant calculated by the time lag method (Crank p 51).

(11) Rogers (1960)

*Polymers.* LDPE (a): High pressure and temperature;  $\rho$ , 0.922; 62%;  $l$ , 0.050. LDPE (b): Zeigler;  $\rho$ , 0.939; 69%;  $l$ , 0.041. LDPE (c): High pressure and temperature;  $\rho$ , 0.919; 60%;  $l$ , 0.533. HDPE: Phillips;  $\rho$ , 0.954; 76%,  $l$ , 0.056.

*Migrants.* Bromomethane, Matheson 99.4%; isobutylene, Matheson, 99.0%; benzene, n-hexane, no data; all dried over sodium and distilled.

*Method.* (1) Steady state permeability measured monometrically. (2) Sorption and desorption isotherms measured gravimetrically.

*Calculation.* (1)  $\bar{D}$  measured from time lag (Crank p 51) and  $\bar{D} = P/S$  from steady state permeation and equilibrium solubility experiments. (2)  $\bar{D}$  measured from linear portions of sorption and desorption curves (Crank p 245) from  $\bar{D} = \pi/32 [K_s^2(0,C) + K_d^2(C,0)]$ . ( $\bar{D}$  values from the three methods were in good agreement).  $D_{c \rightarrow 0}$  was obtained from  $\bar{D} = D_{c \rightarrow 0} \exp(\gamma\alpha)$  where  $\alpha = p/p_0$ . Data obtained from Table 4.

*Note.*  $\gamma$  values in (g/g): LDPE (a): Isobutylene, 65; benzene, 55; n-hexane, 45. LDPE (b): Bromomethane, 53; n-hexane, 110. LDPE (c): Bromomethane, 12. HDPE: n-hexane, 150; bromomethane 70.

(12) Gray (1973)

*Polymer.* LDPE: Eastman Tenite 800E;  $\rho$ , 0.917.

*Migrants.* Benzene, n-decane, n-tetradecane, no data.

*Method.* Inverse gas chromatography, column packed with 40-60 mesh glass beads coated with polymer,  $0.755 \times 10^{-4}$  cm thick.

*Calculation.* Diffusion constant calculated from the Van Deemeter equation with  $8/\pi^2$  replaced by  $2/3$ .  $D$  and  $E$  data for n-tetradecane obtained from Arrhenius plots of data in Table 2.  $D$ 's for n-decane are from smoothed curve of Table 2 data.

*Note.* Some oxidation of LDPE probably occurred with n-tetradecane (private communication, D. G. Gray).

(13) Aboul-Nasr (1979)

*Polymer.* LDPE: as in (14) Fels (1970b).

*Migrants.* Benzene, n-hexane and n-heptane; Fisher Scientific Co., spectroscopically pure, reagent grade.

*Method.* Adsorption measured gravimetrically in a steady stream of vapour at constant temperature and pressure.

*Calculation.* Equations developed by Fels (1970a) for the Fujita free volume model for unsteady state diffusion into and from an infinite sheet (Crank p 243) were fitted to data by successive approximations and parameters containing  $D_{c \rightarrow 0}$  and the free volume were determined. Data for  $D_{c \rightarrow 0}$  and  $E$  are taken from Tables 1, 2 and 3 of Aboul-Nasr (1979b).

*Note.*  $D_{c \rightarrow 0}$  was found to increase with solvent pretreatment and decrease upon irradiation with  $\text{Co}^{60}$   $\gamma$ -ray in vacuum.

(14) Fels (1970)

*Polymer.* LDPE: from Canadian Ind. Ltd.;  $\rho$ , 0.916; 54%;  $MI$ , 7.0 g/10 min. (% unaffected by soaking at 35-45°C in benzene or n-hexane).

*Migrants.* Benzene, n-hexane, no data.

*Method.* Desorption measured gravimetrically for sheet brought to equilibrium sorption by contact with liquid migrant.

*Calculation.* Dependence of  $D$  on swelling corrected by Fujita free volume model for unsteady-state diffusion from an infinite sheet.  $D_{c \rightarrow 0}$  and free volume parameters obtained from numerical solutions of:

$$\frac{\partial c}{\partial t} = \frac{\partial}{\partial x} \left\{ (1-V)^2 \exp\left(\frac{V}{a+bV}\right) \frac{\partial c}{\partial x} \right\}$$

where  $a$  and  $b$  involve a free volume parameter and  $D$ , and  $V$  is the volume fraction of migrant. (See Crank p 243).

*Note.*  $D_{c \rightarrow 0}$  decreases with  $\text{Co}^{60}$   $\gamma$ -ray grafting of polystyrene onto the LDPE.

(15) McCall (1958)

*Polymer.* LDPE: 'DYNK' from Bakelite Div. of Union Carbide; 70%. HDPE: Marlex 50, Phillips Petroleum; 95%

*Migrants.* Benzene, Merk, reagent grade; hexane-2, n-hexane, Phillips, 95%; *p*-dioxane, Eastman Kodak, D. P. Div.; cyclohexane, 3 methyl pentane, 2,2 dimethylbutane, n-octane and n-decane, Phillips, 99%; carbon tetrachloride, Allied Chem., reagent grade.

*Method.* Desorption and time lag permeability measured gravimetrically in separate experiments.

*Calculations.* Diffusion into an infinite sheet with concentration dependence given by  $\gamma$  was numerically integrated, computed and compared with desorption curves—see McCall (1957).

*Notes.*  $E$  and  $D$  at saturation are given in McCall (1958). Values for  $D_{c \rightarrow 0}$  at 25°C in McCall (1957) for LDPE are about 10X comparable values for HDPE.  $D_{c \rightarrow 0}$  and  $E$  from time lag are, in general, larger than values from desorption.

(16) Barrer (1958)

*Polymer.* LDPE: Alkathene, ICI Plastic Div.;  $\rho$ , 0.920;  $M_v$ , 16 500.

**Migrant.** Benzene, reagent grade, treated with mercury, washed, filtered, distilled, twice fractionally crystallized and dried over sodium.

**Method.** Time lag permeation measured manometrically.

**Calculation.** Assumed  $D$  and time lag were functions of concentration only (Crank p 51).  $D$  extrapolated to zero volume fraction of migrant (Crank, eq. 10.84, pp 223–224).

(17) Durrill (1969)

**Polymer.** LDPE: PP, no data.

**Migrants.** Chlorodifluoromethane, no data.

**Method.** Sorption measured manometrically after pressure jumps up to 300 atm.

**Calculation.** Concentration independent diffusion into an infinite sheet (Crank, p 24, eq. 2.67). Time–pressure curves fitted to equation by trial and error.  $D$  was fairly independent of pressures below 20 atm. Data extrapolated from 188.3°C to 190°C assuming  $E = 10 \text{ kcal mol}^{-1}$ .

(18) Trifonov (1975)

**Polymer.** LDPE: Kalle (FGR);  $l$ , 0.15.

**Migrant.** Ethylacetate, no data.

**Method.** Attenuated total reflection infra-red spectroscopy.

**Calculation.** Concentration independent diffusion into an infinite sheet from a constant surface concentration (Crank p 24) was assumed. Concentration, as a function of distance, was calculated from an equation by Memming relating it to incident and reflected light intensities. Data extrapolated from 36°C to 40°C assuming  $E = 15 \text{ kcal mol}^{-1}$ .

(19) Sobolev (1957)

**Polymer.** LDPE:  $\rho$ , 0.922;  $l$ , 0.038 and 0.5.

**Migrants.** Bromomethane, Matheson, 94.4%.

**Method.** High vacuum permeability measured monometrically.

**Calculation.** Concentration independent diffusion constants were calculated by the time lag method (Crank p 51). Data for  $\bar{D}$  from Figure 7 were plotted to obtain  $E$  and  $A$ .  $\bar{D}$  values at 0° and 10°C deviated from Arrhenius plot.

(20) Michaels (1962)

**Polymer.** LDPE: Bakelite, Union Carbide Corp.;  $\rho$ , 0.918;  $l$ , 0.004. HDPE: Grex, W. R. Grace;  $\rho$ , 0.957;  $l$ , 0.008.

**Migrants.** *o*-xylene, *p*-xylene, Eastman Kodak, reagent grade.

**Method.** Steady state permeation into a vacuum measured by trapping and weighing vapour. Solubilities measured gravimetrically for equilibrium uptake from liquid migrants.

**Calculation.**  $\bar{D}$  calculated from steady state rate of permeation and equilibrium solubility (Crank, Ch 4). Data were calculated from Arrhenius curves in Figure 4.

(21) Sefton (1979)

**Polymers.** (All are Sclair Polyethylene Resins): LDPE (a): (No. 8107);  $\rho$ , 0.925; 50%  $MI$ , 4.6. LDPE (b): (E341–01);  $\rho$ , 0.932; 55%  $MI$ , 3.0. LDPE (c): (No. 8507);  $\rho$ , 0.939; 59%  $MI$ , 5.4. HDPE (a): (No. 8707);  $\rho$ , 0.948; 65%  $MI$ , 5.3. HDPE (b): (No. 2908);  $\rho$ , 0.961; 74%  $MI$ , 7.1. (all films;  $l$ , 0.2).

**Migrants.** 2,2',4 trimethylpentane, no data.

**Method.** Sorption and desorption measured gravimetrically.

**Calculation.** Concentration independent diffusion constant into an infinite sheet from at constant surface concentration were calculated for small times (Crank p 48).  $\bar{D}$  was calculated from initial rates of reduced mass vs.  $t^{1/2}l^{-1}$  curves (Crank pp 244–246).  $\bar{D}$  extrapolated from 54° to 50°C assuming  $E = 15 \text{ kcal mol}^{-1}$ .

(22) Braun (1976)

**Polymer.** LDPE: Eastman Kodak 800E;  $\rho$ , 0.917.

**Migrants.** Tetralin, tert-butyl-4-hydroxy anisole (BHA), and 2-5 ditertbutyl-4-hydroxy toluene (BHT), Eastman Kodak; *n*-dodecane, Polysciences; and *cis* and *trans*decalin, separated by g.c.

**Method.** Inverse gas chromatography; column packed with 60–80 mesh gas beads coated with polymer,  $2.0 \times 10^{-4} \text{ cm}$  thick.

**Calculation.**  $D$  calculated from VanDeemter equation with  $8/\pi^2$  replaced by  $2/3$  (see Millen 1977). Data for diffusion parameters obtained from Arrhenius plots.

(23) Westlake (1975)

**Polymer.** LDPE: Moulded at 150°C, cooled at 10–20 K  $\text{min}^{-1}$ ;  $\rho$ , 0.920;  $M_1$ , 25 600;  $M_2$ , 679 400, 43%. HDPE: Moulded at 180°C; cooled fairly rapidly;  $\rho$ , 0.960;  $M_1$ , 5500;  $M_2$ , 120 000; 68%. PP: Moulded at 200°C; cooled at 10–20 K  $\text{min}^{-1}$ ;  $\rho$ , 0.900;  $M_1$ , 91 700;  $M_2$ , 266 500; 65%. HDPE/03PP copolymer: Moulded at 180°C; cooled 10–20 K  $\text{min}^{-1}$ ;  $\rho$ , 0.955;  $M_1$ , 5500;  $M_2$ , 120 000; 72%.

**Migrants.** Radioactive 2,4 dihydroxybenzophenone, synthesized and recrystallized to obtain pale yellow needles, m.p., 144.5–147°C.

**Method.** Rate of migration of radioactive diffusant, deposited on one side of 1 mm thickness disc, measured by counting opposite side. Both low concentration and 'saturated surface' conditions were used.

**Calculation.** Non-steady state concentration independent diffusion through and infinite sheet was assumed. Concentration was obtained from count corrected by Lambert Law extinction coefficient proportional to polymer density. Twenty-five per cent variation found in 0.7 to 10.0 wt% migrant range.  $D$  (saturated conditions) for constant surface concentration (Crank p 47);  $D$  (non-saturated Conditions) for impermeable surfaces, one initially zero concentration (Crank p 63). Data points obtained from Arrhenius curves in Figure 3.

(24) Yushkevichyute (1965)

*Polymer.* LDPE: High pressure, dissolved in toluene, precipitated by ethyl alcohol, compression moulded at 100°C,  $M$ , 57 800;  $l$ , 1.5.

*Migrants.* 2-5 ditertbutyl-4-hydroxytoluene ( $^{14}\text{C}$  tagged 'Ionol').

*Method.* Radioactive tracer method; see (54) Gromov (1962).

*Calculation.* Intensity ratio vs.  $t^{-\frac{1}{2}}$  was Fickian and  $D_{c \rightarrow 0}$  was calculated from initial slopes; see (54) Gromov (1962). Data is from an Arrhenius plot.

*Note.* Stretching increased  $D$ ; stretching and annealing increased  $D$  even more.

(25) Gromov (1965a)

*Polymer.* LDPE: High pressure, granular grade PE500, compression moulded at 150°C;  $l$ , 0.15 to 0.20, Williams plasticity (height of specimen under load of 0.86 mm). PP: Atactic; from a commercial product by ether extraction; cast from solution on mercury surface. PIB: From a commercial product (Grade P-85) by fractional precipitation, films cast from solution on mercury;  $M_v$ ,  $2.5 \times 10^5$ ,  $l$ , 0.15 to 0.20.

*Migrants.* n-octane, n-dodecane, n-hexadecane, ceresin ( $M \sim 225$ ), polyethylene ( $M \sim 2000$ ), polyethylene ( $M \sim 5000$ ), paraffin (325), no data.

*Method.* Interference micromethod was used.

*Calculation.* Concentration-distance curves appeared to be Gaussian and were analysed by the Boltzman-Matano method (Crank pp 231f). Unidirectional diffusion coefficients were calculated from the interdiffusion coefficient,  $D^V$ .  $D$  was calculated from  $D = D^V (1 - V)^{-1}$ , where  $V$  is the volume fraction of migrant. In obtaining  $D_{V \rightarrow 0}$  and  $D_{V \rightarrow 1}$ , account was taken of the change in activation energy with concentration. Data were taken from Figures 2, 4a and 4b.

(26) Klein (1979)

[(See also Klein (1975), (1976), 1977)].

*Polymer.* LDPE: ICI Plastics Division (WNC17);  $M_2$ ,  $1 \times 10^5$ ;  $M_1/M_2$ , 5;  $\text{CH}_3$ , 30; MP,  $\sim 107^\circ\text{C}$ . HDPE: RAPRA (standard batch HP PEI);  $M_2$ ,  $1.6 \times 10^5$ ;  $M_2/M_1$ , 16;  $\text{CH}_3$ , <1.

*Migrants.* Tetradecaneamide, hexadecaneamide, octadecaneamide; Fluka (purum grade, 99.9%); dodecanyl dodecanate, doconsanyl doconsanate, octadecanyl octadecanate; Pfalz and Bauer, 99%; Five fractions of linear 98% deuterated PE from D. G. Ballard and G. Langnur of ICI: HDPE1,  $M_2$ , 3600;  $M_2/M_1$ , 2.25; HDPE 2,  $M_2$ , 4600;  $M_2/M_1$ , 2.2; HDPE 3,  $M_2$ , 11 000;  $M_2/M_1$ , 3.4; HDPE 4,  $M_2$ , 17 000;  $M_2/M_1$ , 2.2; HDPE 5,  $M_2$ , 23 000;  $M_2/M_1$ , 1.8.

*Method.* Uniform dispersion of diffusant within polymer matrix either by melt blending for 20 min at 160°C or precipitation from mutual solution in *p*-xylene (for HDPE's) to obtain concentrations in the range, 0.5 to 2.0% (g/g.). Cylindrical pellets of the polymer and polymer/diffusant moulded at 155°C were joined by melting surfaces in vacuum. After diffusion in inert

atmosphere, quenched specimens were microtoned and concentration profiles obtained by infra-red microdensometry.

*Calculation.* Concentration independent diffusion was determined by fitting a step function to experimental curves and equation  $c(x,t) = 1/2 C_0 \operatorname{erfc} [x/2(Dt)^{1/2}]$ . Amide values were obtained from Figure 6 of Klein (1979) where ordinate values of inset are in error by a factor of 10. Values of  $D$  for the esters were obtained from Figures 7, 8 and 9 and from Table 2 of Klein (1977). Separate Arrhenius parameters were calculated below and above the melting temperatures of PE. Diffusion constants for dodocanyl dodecanate and doconsanyl doconsanate were also obtained in rapid cooled and annealed HDPE. In the case of HDPE's, a modified diffusion constant which takes into account the effect of molecular weight distribution of the migrant on the concentration profiles was calculated. The latter  $\bar{D}$  values were extrapolated from 176 to 180°C assuming an activation energy of 6.7 kcal mol $^{-1}$ .

(27) Cicchetti (1968)

*Polymer.* LDPE: Fertene Q/1, high pressure from Montecatini-Edison S.p.A.; 59% VIS, 0.95 (135°C, Tetralin). HDPE: Rotene 10/Q, linear Ziegler-Natta, from Montecatini-Edison, S.p.A.; 70%; VIS, 1.40 (135°C, tetralin). Low crystallinity PP: From Ziegler-Natta by extraction with boiling heptane, 90% soluble in boiling ethyl ether; 16%; VIS., 0.30 (135°C, tetralin). Stereoblock PP: From Ziegler-Natta by hexane extraction; 24%; VIS, 0.59 (135°C, tetralin).

*Migrants.* 2-Hydroxy-4-methoxy benzophenone, 2 hydroxy-4-n-butoxy benzophenone, 2-hydroxy-4-n-octoxybenzophenone, 2 hydroxy 4-n-dodecoxybenzophenone, 2-hydroxy-4-n-octadecoxy benzonphenone, dimethyl-3,3'-thiodipropionate and dihexyl-3,3'-thiodipropionate. See (55) Dubini (1967).

*Method.* An undisclosed quantity of radioactive migrant was placed at the end of a cylinder of polymer and heated 16-20 h. Cylinder was sectioned and the radioactivity of the slices determined.

*Calculation.* Concentration independent diffusion from unsaturated initial conditions through an infinite cylinder (Crank p 12), time of solution  $\ll$  time of diffusion. No data given on initial amounts of migrants or their solubilities. Initial concentration is equal to 'total amount of diffusing substance divided by the cross-section of the cylinders'. Measured concentrations range about 1-2%. Diffusion constants calculated from Arrhenius parameters in Table 1.

(28) Auerback (1958)

*Polymer.* LDPE: Bakelite (DXL-14). PIBa: Enjay 17-100;  $\rho$ , 0.914; VIS, 1.63 (benzene, 30°C). PIBb: Enjay L-100; VIS, 1.42 (benzene, 30°C). HPBD: Hydropol V (Phillips) C=C, 50;  $\rho$ , 0.894; VIS, 0.55 (benzene, 30°C).

*Migrants.* n-octadecane, octadecanol, octadecyl octadecanate, octadecanoic acid (dimer), no data.

*Method.* Uniform dispersions of tagged migrant and polymer were cast from benzene, dried, rolled, and pressed into sheets ( $l$ ; 0.03). Two sheets, one with 1.3 to 1.5% migrant, other 0% migrant, were placed in intimate

contact and point at zero concentration surface monitored.

*Calculation.* Concentration independent non-steady state diffusion into an infinite sheet obtained by method in (Crank, p 49). Data obtained from Arrhenius plots of data in Table 2.  $D$  found to be concentration independent for concentrations of 1.5 to 4.3% g/g.

(29) Thinius (1964)

*Polymer.* LDPE: Suprathen;  $l$ , 0.30. HDPE: (V-50);  $l$ , 0.025. PP: (unfilled)  $l$ , 0.025.

*Migrants.* Dibutylphthalate, tricresylphosphate, bis (2-ethyl hexyl) phthalate, no data.

*Method.* Diffusion into polymer sheet from a contiguous sheet of PVC 65%/migrant 35% W/W was measured gravimetrically.

*Calculation.*  $D$  was measured from the initial slope of  $\Delta m$  vs.  $t^{1/2}$  plots. Arrhenius parameters were calculated from Table 1.

(30) Gromov (1965b)

*Polymer.* See (25) Gromov (1965a).

*Migrants.* Paraffin, homogenized, 22–25 carbon atoms; MP, 51°C; index of refraction (60°C,  $D$ ) 1.4334.

*Method.* See (25) Gromov (1965a).

*Calculation.* See (25) Gromov (1965a), values calculated from table on p 805.

(31) Johnson (1975)

*Polymer.* See (23) Westlake (1975).

*Migrants.* Radioactive 2-hydroxy-4-octoxy benzophenone synthesized from migrant in (23) Westlake (1975) and recrystallized to obtain pale yellow product (m.p. 47.5°–48.5°C).

*Method.* See (23) Westlake (1975).

*Calculation.* See (23) Westlake (1975), data points obtained from Arrhenius curves in Figure 2.

(32) Jackson (1968)

*Polymer.* LDPE:  $M_2$ ,  $7.3 \times 10^5$ ;  $CH_3$ , 26.5; 54%; C=C, 0.035; CO, 0.017; VIS, 1.26 (decalin, 135°C). PP:  $M_2$ ,  $3.5 \times 10^5$ ; 60%; VIS, 2.6 (decalin, 135°C). PMP:  $M_2$ ,  $8.6 \times 10^5$ ; 53%; VIS, 2.0 (decalin, 135°C).

*Migrants.* *N*-octadecyl-diethanolamine, didocdecyl 3,3'-thiodipropionate and 1,1,3 tri[2 methyl-4 hydroxy-5 (t-butyl) phenyl] butane were synthesized, recrystallized and purified by chromatography.

*Method.* Radioactive migrant solution evaporated into shallow wells of polymer discs—count of initially inactive surface measured as a function of time.

*Calculation.* (1) Concentration independent diffusion into an infinite sheet with the layer assumed to be an impermeable surface (Crank pp 63, 252) with  $D$  calculated from the intercept of (Crank, eq. 10.160). (2) Diffusion modelled by a perfectly stirred liquid (Crank p 239) gave slightly higher  $D$  values but was not used.  $D$  calculated from Arrhenius plots of data in Table 2.

(33) Gromov (1965c)

*Polymer.* See (25) Gromov (1965a).

*Migrants.* Ceresin:  $M_1$ , ~450; a mixture of branched saturated hydrocarbons synthesized from carbon monoxide and hydrogen. Ceresin:  $M_1$ , ~600; obtained from processing of ozokerite, a natural wax; probably more branched than Ceresin (450).

*Method.* See (25) Gromov (1965).

*Calculation.* See (25) Gromov (1965a)  $D$  from Arrhenius plots of data in table.

(34) Lundberg (1964)

*Polymer.* HDPE: Phillips, Marlex 6050.

*Migrants.* Methane, see (5) Lundberg (1962).

*Method.* See (5) Lundberg (1962).

*Calculation.* See (5) Lundberg (1962).

(35) Eby (1964)

*Polymer.* HDPE:  $\rho$ , 0.970;  $CH_3$ , 1.7; slowest cooling from melt and annealed.

*Migrants.* Ethane, no data.

*Method.* Sorption measured gravimetrically at 0.5 atm.

*Calculation.* Concentration independent steady state diffusion into an infinite sheet (Crank, Ch. 4).

*Notes.*  $D$  was faster in the surface layer of rapid cooled samples than in their interior.  $D$ 's for interior of all samples were  $1-2 \text{ cm}^2 \text{ s}^{-1} \times 10^{-8}$ .  $D$  at 23°C was extrapolated to 25°C assuming  $E = 13 \text{ kcal mol}^{-1}$ .

(36) Michaels (1964)

*Polymer.* HDPEa: Grex, Grace Co. by Phillips process;  $\rho$ , 0.952;  $M_2$ , 119 000;  $CH_3$ , 1.5;  $l$ , 0.2 to 1.0; moulded in press at 150°C; rapid cooled and annealed at 130°C. HDPEb: Same as 'a' except  $\rho$ , 0.969; moderately cooled and annealed at 130°C.

*Migrant.* Ethane, no data.

*Method.* Time lag permeation measured manometrically.

*Calculation.* Concentration independent  $\bar{D}$  calculated by time lag method (Crank p 51, eq. 4.26)  $\bar{D}$  from time lag was in good agreement with  $\bar{D}$  from permeation. Data calculated from Arrhenius plots, Figures 1 and 7.

*Note.*  $D$  was found to be inversely proportional to crystallinity induced by cooling rate.  $D^*$  for 100% amorphous at 25°C was extrapolated to be  $40 \times 10^{-8} \text{ cm}^2 \text{ s}^{-1}$ ; annealing increased  $\rho$  but did not decrease  $\bar{D}$ . Thermal effects not related to changing  $\rho$  affected  $\bar{D}$  values.

(37) Lowell (1971)

*Polymer.* HDPE: Dupont, PE-85;  $M_2$ ,  $1.44 \times 10^5$ ;  $CH_3$ , 1,  $MI$ , 2.92. HDPE: B. P. Plastics, Rigidex Type 2,  $M_2$ ,  $1.7 \times 10^5$ ;  $CH_3$ , 1;  $MI$ , 0.2. Two samples are not distinguished in text;  $\rho$  (annealed at 124°C), 0.965, data is for sample with  $l$ , 0.24; slow cooled, annealed at 124°C and crosslinked by 10 mrad  $^{60}\text{Co}$   $\gamma$  irradiation.

*Migrants.* Ethane, 99%; cyclopropane, 99.9%; n-butane,

99.99%; 2 2'-dimethylpropane, 99.87%; all from Air Products Ltd.

*Method.* Sorption on a sheet measured gravimetrically.

*Calculation.* Concentration independent  $D$  for diffusion into an infinite sheet (Crank p 239). Relaxation time obtained from slopes of  $[M(\infty)-M(t)]/M_\infty$  vs.  $t$ . No pressure dependence on  $D$  below 400 torr. Data for ethane are from Figure 3, for  $l$ , 9; moderately cooled, annealed, surface layer not removed; cyclopropane,  $\leq 120^\circ\text{C}$ , Figure 5; cyclopropane  $\geq 140^\circ\text{C}$ , n-butane and neopentane data calculated from Table 4.

*Note.*  $D$  independent of  $^{60}\text{Co}$  irradiation,  $D$  decreased  $\sim 10\%$  upon removal of surface layer, however  $D$  also decreases as thickness decreases;  $D$  (quenched, annealed)  $\gg D$  (slow cooled, annealed).

(38) Peterlin (1967)

*Polymer.* HDPE: Celanese Fortiflex A-60-500;  $\rho$ , 0.945;  $M_1$ , 5500;  $M_2$ , 80 000; 68%;  $l$ , 0.5; compression moulded at  $150^\circ\text{C}$ . Results are for samples quenched from melt in ice water (annealed samples,  $\rho$ , 0.970; 81%).

*Migrants.* Methylchloride, no data.

*Method.* Sorption measured gravimetrically.

*Calculation.*  $D$  determined from  $W_t/W_\infty$  vs.  $t^{1/2}$  which was linear below 0.5% W/W.  $D_{c \rightarrow 0}$  determined from extrapolation with  $\gamma(25^\circ\text{--}55^\circ\text{C})=25.0$  g/g. Values for  $25^\circ\text{C}$  and  $35^\circ\text{C}$  for  $D_{c \rightarrow 0}$  from Figure 5 were used. These do not correspond to  $\bar{D}_{c \rightarrow 0}$  values from the Arrhenius plot used for  $D_{c \rightarrow 0}$  values at  $40^\circ\text{--}60^\circ\text{C}$  in Figure 6.

*Notes.* Cold draw ratio of 8 decreased  $D$  at  $25^\circ\text{C}$  to  $0.2 \times 10^{-8} \text{ cm}^2 \text{ s}^{-1}$ . Draw ratio of 9, to  $0.010 \times 10^{-8} \text{ cm}^2 \text{ s}^{-1}$  [Williams (1971)]. Draw ratio of 2 in benzene increased  $D$  at  $25^\circ\text{C}$  to  $178 \times 10^{-8} \text{ cm}^2 \text{ s}^{-1}$  [Williams (1970)].

(39) Baddour (1964)

*Polymer.* HDPE: W. R. Grace Co. Cast linear films;  $\rho$ , 0.942;  $l$ , 0.25.

*Migrants.* *o*-xylene, *p*-xylene, *cis* 1,2-dichloroethylene, *trans* 1,2-dichloroethylene, no data.

*Method.* Same as (20) Michaels (1962) except that flux was measured volumetrically as well as gravimetrically.

*Calculation.* Same as (20) Michaels (1962).  $\bar{D}_c$  was calculated from permeation flux at unit thickness where  $\bar{D}_c$  is the integral diffusivity for a sheet at equilibrium concentration of migrant,  $C$ , at one face and evacuated on the other (Crank Ch. 4). Values of  $D$  and  $E$  were calculated from Arrhenius fit of Figure 7;  $D_{c \rightarrow 0}$  values, from Table 5.

*Notes.* Annealing to as high as  $115^\circ\text{C}$  increased  $\bar{D}$  as much as 30%; *p*-xylene treatment to as high as 30% concentration at  $97^\circ\text{C}$ , increased  $\bar{D}$  as much as 70–160%. ( $C_{c \rightarrow 0}$  was determined from  $\bar{D}_{c \rightarrow 0} = D_{c \rightarrow 0} \exp(\gamma C / \rho_1 \alpha)$  where  $\rho_1$  = migrant density and  $\alpha$  = amorphous fraction);  $\gamma$  (*o*-xylene), 2.5;  $\gamma$  (*p*-xylene), 2.8;  $\gamma$  (*trans* 1,2-dichloroethylene), 1.3;  $\gamma$  (*cis* 1,2-dichloroethylene), 1.1, at  $30^\circ\text{C}$ .

(40) Michaels (1969)

*Polymer.* HDPE: 60%, no other data. *PP*: Hurcules

Profax-6520F;  $\rho$ , 0.905;  $M_2$ ,  $3 \times 10^5$ ; 65%,  $l$ , 1.3; 95% isotactic; hot cast and rolled at  $110^\circ\text{C}$ .

*Migrants.* *p*-xylene, *o*-xylene, toluene, methycyclohexane; 2,2',4-trimethylpentane; reagent grade.

*Method.* Same as (20) Michaels (1962) except cell was weighed periodically and an air-stream was used on the down stream side.

*Calculation.* Same as (20) Michaels (1962).

(41) Blackadder (1974)

*Polymer.* HDPE: B. P. Chemical Rigidex 50;  $\rho$ , 0.955;  $M_2$ , 80 000;  $M_2/M_1$ , 5; compression moulded at  $145^\circ\text{C}$  and cooled to  $50^\circ\text{C}$  at  $10^\circ\text{C/h}$ , 0.66% W/W soluble in xylene at  $40^\circ\text{C}$ ;  $l$ , 0.045–0.177.

*Migrants.* *p*-Xylene, 99%, Imperial Ind. Ltd., contaminants mainly isomers.

*Method.* Sorption and desorption measured gravimetrically at vapour activities from 0.076 to 0.92 ( $p/p_0$ ) see Blackadder (1973).

*Calculation.* Concentration independent diffusion into an infinite sheet was used as a model.  $D_{ab}$  and  $D_{des}$  were calculated from slope of sorption–desorption curves using (Crank, eq. 10.160, pp 238–239).  $\bar{D}$  was calculated from the average from  $\bar{D}_{ab}$  and  $\bar{D}_{des}$  (Crank, p 244). Datum from Table 1 is an average  $\bar{D}$  for 0.39 activity (at 0.92 activity,  $\bar{D} = 2.4 \times 10^{-8} \text{ cm}^2 \text{ s}^{-1}$  at  $30^\circ\text{C}$ ).

(42) Prager (1951b)

*Polymer.* PIB: Enjay Co., Vestanex B-100;  $\rho$ , 0.910;  $M_v$ ,  $10^6$ ; 80% reprecipitated from benzene/acetone; cast from cyclohexane, leached with methanol and dried in vacuum at  $45^\circ\text{C}$ ;  $l$ , 0.08 to 0.36.

*Migrants.* Propane, no data.

*Method.* Sorption and desorption measured gravimetrically, cycling between vacuum and vapour pressures from 32 to 1460 mm.

*Calculation.*  $\bar{D}$  obtained from initial slopes of sorption and desorption plots (Crank p 238 f)  $\bar{D}_{c \rightarrow 0}$  calculated  $\gamma(35^\circ) = 24.6$  g/g; datum from Table 2.  $\bar{D}_{c \rightarrow 0}$  extrapolated from  $35^\circ$  to  $30^\circ\text{C}$  assuming  $E = 17 \text{ kcal mol}^{-1}$ .

(43) Prager (1953)

*Polymer.* PIB: see (42) Prager (1951b).

*Migrants.* n-butane, isobutane, n-pentane, 2 methylbutane, 2,2-dimethylpropane, no data.

*Method.* See (42) Prager (1951b).

*Calculation.* As in Prager (1951b) and checked with a step function method, Prager (1951a).  $\bar{D}_{c \rightarrow 0}$ ,  $E$  and  $A$  were obtained from Arrhenius plots of data in Table 1.  $\gamma$ (g/g) (average  $25^\circ$  to  $46.5^\circ\text{C}$ ): n-butane, 25.5; isobutane, 23.8; n-pentane, 24.4; isopentane, 22.6; neopentane, 16.1.

(44) Blyholder (1960)

*Polymer.* PIB: As described in (42) Prager (1951b).

*Migrants.* n-pentane, methylcyclopentane, n-hexane, 2-methylpentane, 3-methylpentane, methylcyclohexane, n-heptane and n-octane, Phillips Petroleum Co., pure grade.



*Method.* Time lag permeation was measured monometrically.

*Calculation.* Concentration independent  $\bar{D}$  calculated by the time lag method (Crank, p 51, eq. 4.26)  $\bar{D}_{c \rightarrow 0}$  obtained by extrapolation of lags to zero pressure. Data were obtained from Arrhenius plots of Table 1.

## (45) Boss (1967)

*Polymer.* PIB: Esso Research Vistanex (L-80);  $M_w$ ,  $1.5 \times 10^6$ ; VIS (24°C, Benzene), 1.02, also PIB, California Research Corp., very sharply fractionated;  $M$ ,  $0.508 \times 10^6$ .

*Migrants.* Benzene, Mallinckrodt No. 3856, reagent grade, redistilled.

*Method.* Pulsed nuclear resonance (Spin-echo) with digital collection.

*Calculation.* Plot based on Fujita–Doolittle theory (see Figure 4), values obtained for  $D$ , the self-diffusion coefficient in the 30–100% range of benzene concentration were extrapolated to zero concentration (no molecular weight distribution dependence on PIB was observed).

## (46) Chen (1968)

*Polymer.* PIB: See (50) Moore (1962).

*Migrants.* n-hexadecane, Nuclear Chicago; n-dodecane, International Chem. and Nuclear Corp. (both diluted with respective non-radioactive hydrocarbons from Matheson, Coleman, Bell, 99%).

*Method.* Thin smear technique, see (50) Moore (1962).

*Calculation.* See (50) Moore (1962), (Crank eq. 10.178) concentration  $< 0.02\%$  so it was assumed  $D_{c \rightarrow 0}$ . Dodecane data was calculated from parameters in Table 1 and hexadecane, from Arrhenius plot in Figure 5.

## (47) Wong (1970)

*Polymer.* PIB: see (50) Moore (1962).

*Migrants.*  $^{14}\text{C}$ -1, 1 diphenylethane, Mallenckrodt Nuclear Corp.; 1, 1diphenylethane, K and K Labs.

*Method.* Thin smear technique, see (50) Moore (1962).

*Calculation.* See (50) Moore (1962), Crank (eq. 10.178); since  $C < 0.02\%$  assumed  $D_{c \rightarrow 0}$ ; data are from Arrhenius plot in Figure 1.

## (48) Secor (1967)

*Polymer.* PIB: Chevron Chem. Co., Oronite 32, highly branched, liquid,  $> 95\%$  isobutylene structure;  $M_1$ , 1400;  $M_2$ , 2500, VIS (25°C), 770 poises.

*Migrants.* 1,1,2 trichloroethane (freon 113) DuPont, 99.9%, VIS (25°C), 0.66 cp.

*Method.* Concentration–distance profiles were determined by microinterferometry. Viscous liquid polymer and polymer–migrant solution were placed in contact.

*Calculation.* Non-steady state, concentration dependent diffusion into an infinite sheet was calculated

from  $D = - \int_0^c xdc/2t(dc/dt)$  by graphical integration and curve fitting the profile.  $D$ , below  $15 \text{ g cm}^{-3}$

concentration, was found to be only slightly concentration dependent.

## (49) Kuzminskii (1964–6)

*Polymer.* PIB: no data.

*Migrants.* Phenyl-2-naphthylamine, no data.

*Method.* Ultraviolet luminescence of migrant used to measure distance of penetration as a function of time.

*Calculation.*  $D = (X^2/4t) [\varphi(1 - 2/v)]^{-2}$ , where  $\varphi$  is the inverse (transform) of the error function and  $v$  is the dilution. Parameters were calculated from an Arrhenius plot of data in Figure 2.

## (50) Moore (1962)

*Polymer.* PIB: Esso Research Vestanex (L-80);  $M_w$ ,  $1.5 \times 10^6$ ; VIS (24°C, benzene), 1.02.

*Migrants.* n-hexadecane, Matheson, Coleman, Bell.  $^{14}\text{C}$ -n-hexadecane, Nuclear Chicago Corp.

*Method.* (1) Twin moulded discs, one with active, other with inactive migrant, both at the same migrant concentration were layered together and the activity measured at the outside of the non-active disc. (2) Thin smear of radioactive migrant pressed to surface of disc;  $l$ , 1.4; activity counted at other surface.

*Calculation.*  $D$  calculated taking into account activity of migrant beneath the surface (Crank p 252, eqs. 10.178, 10.179).  $D_{c \rightarrow 0}$  obtained from Arrhenius plot of Table 1 for thin smear (100% polymer) data.

## (51) Park (1957)

*Polymer.* PIB: ICI, Billingham;  $M$ , 92000; reprecipitated from benzene/carbon tetrachloride; cast from solution;  $l$ , 0.77.

*Migrants.*  $^3\text{H}$  labelled and normal 2-methylbutane and 2-methylbutane prepared respectively from  $^3\text{H}_2\text{O}$  and  $\text{H}_2\text{O}$  by Grignard and purified.

*Method.* Exchange between radioactive and non-radioactive migrant followed by monitoring the increasing activity of the vapour phase.

*Calculation.* Self diffusion coefficient,  $D^*$ , was measured (Crank, p 56). Its value was obtained by extrapolation to zero per cent regain in Figure 3 and then extrapolated from 35° to 30°C assuming  $E = 17 \text{ kcal mol}^{-1}$ .

## (52) Fensforff (1964)

*Polymer.* PP: Atactic from extraction with boiling heptane of a PP made with titanium trichloride–triisobutylaluminum catalyst, then extraction of about 27% by boiling ether; 10% ( $\rho$  and i.r.).

Ethylene–propylene copolymers: Prepared in perchloroethylene with a vanadium oxychloride–triisobutylaluminum catalyst; non-crystalline-rubbery;  $M$ ,  $> 100000$ ; % polyethylene determined by i.r. and with  $^{14}\text{C}$ -ethylene, ethylene/propylene ratio given in mole per cent; films cast from solvent and exposed to solvent until shrinkage ceased;  $l$ , 0.1 to 0.4.

*Method.* Sorption and desorption measured gravimetrically.

Calculation.  $\bar{D} = 1/2(\bar{D}_{ad} + \bar{D}_{des})$  from weight vs.  $t^{1/2}$  plots were extrapolated to  $D_{c \rightarrow 0}$ . Values from final desorption values are given. Data for benzene in copolymers are taken from the Arrhenius plot in Figure 6. Values for  $D_{c \rightarrow 0}$  for the other migrants were extrapolated from 23° to 25°C assuming  $E = 15 \text{ kcal mol}^{-1}$ .

(53) Long (1965)

Polymer. PP: 74%.

Migrants. Toluene, methylcyclohexane, n-heptane, no data.

Method. Desorption measured gravimetrically.

Calculation.  $D_{c \rightarrow 0}$  measured from limiting desorption on log w vs. t plot (Crank p 246). Data obtained from Arrhenius plot in Figure 6.

(54) Gromov (1962)

Polymer. PP: Solid, isotactic.

Migrants. 2,5-ditertbutyl-4-hydroxytoluene, phenothiazine, no data.

Method. 'Thick layer' method used, viz., polymer disc,  $l$ , 0.1–0.2, coated with small amount of isotopically labelled migrant. Decrease in activity of coated side is measured.

Calculation.  $D_{c \rightarrow 0}$  was obtained, assuming concentration independent diffusion into an infinite sheet (Crank p 13) from the initial slopes of a reduced intensity vs.  $t^{-1/2}$  plot. Data were obtained from the Arrhenius plot in Figure 2.

(55) Dubini (1967)

Polymer. PP: Isotactic; 63%; VIS (135°C, Tetralin), 3.0; residue after boiling heptane extraction, 96.8%.

Migrants. Dimethyl 3,3'-thiodipropanoate, di-n-hexyl 3,3' thiodipropanoate, di-n-dodecyl 3,3'-thiodipropanoate, di-n-hexadecyl 3,3'-thiodipropanoate, 2-hydroxy-4-methoxy-benzophenone, 2-hydroxy-4-n-butoxybenzophenone, 2-hydroxy-4-n-benteophenone, 2-hydroxy-4-n-dodecoxybenzophenone, 2-hydroxy-4-n-octadecoxy benzophenone, no data.

Method. See (27) Ciccetti (1968).

Calculation. See (27) Ciccetti (1968); Diffusion constants are calculated from Arrhenius parameters listed on p 475.

(56) Fishman (1955)

Migrant/polymer. n-pentane-<sup>3</sup>H and n-hexane-<sup>3</sup>H synthesized by reduction of pentene-2 and hexene-2, Phillips Co. (Pure Grade) over platinum; n-pentane, n-hexane, Phillips (Pure Grade).

Method. Diffusion of tritium-labelled specimen from a capillary into a reservoir of non-active specimen. Count of material in the capillary was monitored.

Calculation. Diffusion from uniform initial distributions, with equal initial surface concentrations were assumed.  $D^*$  obtained from  $A_d/A_0 = (\pi^2/8) \exp(\pi^2 D^* t / l^2)$  (Crank p 48);  $D^*$  values calculated from Arrhenius parameters.

(57) Douglas (1958)

Migrant/polymer. n-pentane, n-hexane, n-heptane, n-octane, n-nonane and n-decane from Phillips Co., pure grade,  $\geq 99\%$ ; n-octadecane from Eastman Kodak; n-dotriacontane from W. L. Hawkins, Bell Lab.

Method. Nuclear magnetic resonance—'Spin Echo' technique.

Calculation.  $D$ , self diffusion coefficients, were obtained using the equation of Carr and Purcell. Data calculated from Arrhenius parameters in Table 1.

(58) McCall (1963)

Migrant/polymer. Isobutylene: Indopol H-35, Indol Chem. Co., broad distribution;  $\rho$ , 0.864;  $M_v$  (dilute solution), 1660;  $M_v$  (melt), 700.

Method. See (57) Douglas (1958).

Calculation. See (57) Douglas (1958); data obtained from Arrhenius plot in Figure 1.

(59) McCall (1959)

Migrant/polymer. HDPE (4100): Fractionated, low pressure PE from L. H. Tung, Dow Chem.;  $M_1$ , 4100. HDPE (5800): Same as above except,  $M_1$ , 5800.

Method. See (57) Douglas (1958).

Calculation. See (57) Douglas (1958); data obtained from Arrhenius plot in Figure 1.

(60) Roe (1974)

Polymer. LDPE: 'DYNK' from Bakelite Div. of Union Carbide; moulded at 170°C;  $l$ , 0.012;  $\rho$ , 0.9175; 48%.

Migrants. 4,4'-thiobis (3-methyl-6-tert-butylphenol), and tetrakis [methylene-3-(3',5'-di-tert-butyl-4-hydroxyphenyl)propionate] methane.

Method. Stacks of 13–27 polymer discs, clamped between 0.21 mm thick discs containing 2% migrant at  $2.1 \times 10^5$  Pa pressure were held at constant temperature in vacuum. Concentration–position profiles were obtained from analysis of weight change in air (induction time calibrated as a function of migrant concentration).

Calculation. Concentration independent diffusion into an infinite sheet from a constant surface concentration (Crank, p 24, eq. 2.67) was assumed. Experimental logarithm concentration vs. reduced distance curves were matched with calculated curves to obtain  $Dt/l^2$ . Data are calculated from fit of points in Figure 5 to Arrhenius equation.

(61) Vieth (1969)

Polymer. PP: Isotactic; 95%; 651 Profax, Hercules Inc.;  $M$ , 320 000; 1% oxidation inhibitors.

Migrant. Tetrafluoromethane,  $> 99.8\%$ , dried over calcium sulphate.

Method. Time lag permeation; pressure increase measured manometrically.

Calculation. Concentration independent diffusion constants were calculated by the time lag method (Crank, p 51, eq. 4.26). Values are from Figure 12, sample 25 (moderately cooled, unannealed). (Rapid or slow cooling

had little effect on  $D$  but  $D$  increased slightly upon annealing.)

(62) Senich (1981)

*Polymer.* HDPE: NBS-SRM 1475;  $\rho$ , 0.9784;  $M_1$ , 18 300;  $M_2$ , 53 100;  $MI$ , 2.07 g/10 min VIS, 0.890 (1 chloronaphthalene, 130°C), 1.010 (1,2,4-trichlorobenzene, 130°C), 1.180 (Decalin, 130°C).

*Migrant.* n-Octadecane, no data

*Method.* Inverse gas chromatography. Column packed with 80–100 mesh glass beads coated from hot xylene solution with  $6.1 \times 10^{-4} - 5.7 \times 10^{-3}$  mass fraction of polymer.

*Calculation.* Van Deemter equation with  $8/\pi^2$  replaced by  $(1/12)(m_2\rho_s/18.75\rho)^{1/2}$  where  $m_2$  is the mass fraction of the polymer phase and  $\rho_s$  is the density of the support particles. (This takes into account an angular geometry of the polymer phase which collects at the contact points of randomly packed glass spheres.  $D$  value is the average of the two loadings in Table 4.

(63) Smith (1981)

*Polymer.* LDPE: NBS-SRM 1456;  $\rho$ , 0.9312;  $MI$ , 1.19 g/10 min; VIS, 0.8132 (1 chloronaphthalene, 130°C), 0.9024 (1,2,4 trichlorobenzene, 130°C), 1.042 (Decalin, 130°C). HDPE: NBS-SRM 1475;  $\rho$ , 0.9784;  $M_1$ , 18 300;  $M_2$ , 53 000;  $MI$ , 2.07 g/10 min; VIS, 0.890 (1 chloronaphthalene, 130°C), 1.010 (1,2,4 trichlorobenzene, 130°C), 1.180 (Decalin, 130°C).

*Migrant.* n-octadecane, no data.

*Method.* Compression moulded sheets were formed at 180°C from polymer powder and labelled n-octadecane. Extraction into a limited volume of octadecane was measured continuously from radioactivity.

*Calculation.* Diffusion from an infinite sheet into a stirred solvent of limited volume (Crank, eq. 4.37) was assumed.  $D$  and Arrhenius parameters were calculated from Table 5D. These represent 0.01% initial migrant concentration for HDPE and 1% initial migrant concentration for LDPE.  $D$  increased and  $E$  decreased with the initial concentration of the labelled migrant in the polymer.

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*Diffusion of organic compounds in polyolefins: J. H. Flynn*

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