

VC - FDA

Non-Migration Level of Vinyl Chloride Monomer in PVC

A. J. HAEFNER and G. A. HUGHMARK

Ethyl Corporation
Baton Rouge, Louisiana

Recent evidence confirms previous findings that VCM in levels of 1 ppb in PVC bottle resins are nonmigratory and that such resins can be produced in commercial quantities.

This is an update on the paper presented at the SPE Meeting in April, 1968. At that time we reported experimental data that indicated a non-migration level of about one ppb VCM in PVC. Our recent work confirms this non-migration level.

EXPERIMENTAL PROGRAM

A three part program was conducted following discussion and review by FDA scientists. All low level VCM analyses in PVC were determined with the FDA analytical method using flame ionization detection.

1. PVC bottle resin was batch steam stripped as a dilute slurry in water at 100°C. Heat up with steam plus strip time at temperature was 1½ h. Intermediate and final samples were filtered and dried at mild conditions prior to duplicate analysis. The experimental data are as follows.

Time (min)	VCM (ppm)
initial	0.0031, 0.0025
15	0.0005, 0.0006
30	0.0006, 0.0005
60	0.0007, 0.0004
final (90)	0.0007, 0.0006

2. PVC bottle resin with an initial VCM concentration of 0.7 ppm was steam stripped as an aqueous slurry at 50, 70, and 100°C to develop diffusion coefficient and activation energy data as a function of temperature and concentration at low VCM levels. Sequential strips for 6 min at 100°C, 45 min at 70°C, and 3.5 h at 50°C were used. Samples were filtered and dried after each strip prior to analysis. Unfortunately, we encountered a problem in the drying procedure with the material from the third strip so that these data are not valid. Similarly, feed analysis for the fourth strip at 50° and 70°C are not available. Experimental data are as follows:

Stripping temp, °C	After first strip	After second strip	After fourth strip	After fifth strip
50	0.025 ppm	0.0074 ppm 0.0113	0.0001 ppm 0.0004	0.0012 ppm 0.0009
70	0.030	0.0040 0.0030	0.0000 0.0008	0.0021, 0.0010
100	0.012	0.0030 0.0019	0.0010 0.0010	
Composite	0.023	0.0120 0.0091		

Feed for the fourth strip at 100°C analyzed 0.0010 and 0.0004 ppm VCM, so a fifth strip was not required at this temperature.

3. Sixteen-ounce PVC bottles with an initial concentration of about 0.0014 ppm VCM were filled with 50 percent aqueous ethanol and stored at 120°F for six weeks and 21.5 weeks prior to analysis of the bottle walls. Bottles from the same batch were filled with vegetable oil and stored at 120°F for six weeks.

Analysis of six bottles from the same batch as was used for storage showed 0.0011, 0.0013, 0.0012, 0.0019, 0.0014, and 0.0013 ppm VCM at the time of filling. Analysis of bottles from this batch six weeks later showed 0.0014 ppm VCM and 0.0018 ppm about twelve weeks later. Also, samples of the ethanol and water for the aqueous ethanol were analyzed to assure that there were no interferences in these on the FID chromatograms. Analysis of six bottles after each of the storage tests showed the following results:

50 Percent aqueous ethanol		Vegetable oil
6 Weeks	21.5 Weeks	6 Weeks
0.0004 ppm	0.0009 ppm	0.0030 ppm
0.0007	0.0012	0.0018
0.0007	0.0005	0.0040
0.0007		0.0060
0.0001		0.0032
0.0013		0.0009
Average	0.00065*	0.00087
		0.0031

* Average of 0.00076 if the 0.0001 ppm analysis is eliminated because of apparent VCM loss during analysis.

DATA INTERPRETATION

Results from the first part of the experimental program demonstrate that VCM is reduced to a concentration of about 0.0006 ppm in PVC resin at 100°C and that no further reduction in VCM occurs with continued steam stripping at this temperature. Results from the second part of the program indicate that the non-migration VCM concentration is about 0.001 ppm and is independent of temperature between 50 and 100°C.

The results from the third part of the program show that the VCM in the PVC bottles filled with 50 percent aqueous ethanol decreased to slightly less than one ppb after six weeks storage at 120°F and then apparently remained constant for the next 15 weeks. This also indicates a non-migration level at about one ppb VCM in PVC. The VCM level in the PVC bottles filled with vegetable oil show a statistically significant increase in apparent VCM in the bottles after six weeks storage at 120°F. We suspect that non-VCM components were absorbed by the bottles from the oil and that these represent interference with the FID analysis.

Interpretation of the data from the second part of the program is complicated by lack of complete data resulting from the problem in the drying procedure. Diffusion coefficients and activation energies can be estimated from the data. The stripping data are analyzed by assuming that the VCM removal is controlled by diffusion from uniform spheres to a boundary with zero VCM. The relationship between the concentration after a period of stripping and the initial concentration is given by:

$$\frac{C}{C_0} = \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{e^{-n^2 \pi^2 D t / a^2}}{n^2}$$

where C_0 = initial concentration, C = concentration at time t , D = diffusivity, and a = particle radius. Generally one or two terms of this equation are adequate for these experiments. The term D/a^2 is useful in calculating the diffusivity from PVC resin data because the particle radius is unknown. This equation is applicable because one week was allowed for equilibration of VCM in the PVC between strips.

Stripping temp, °C	D/a^2 (s ⁻¹)		
	First strip	Second strip	Third strip
50	2.28×10^{-3}	3.74×10^{-3}	No valid data
70	9.96×10^{-3}	5.21×10^{-3}	No valid data
100	1.01×10^{-2}	4.91×10^{-3}	No valid data

Prior data obtained with high VCM levels in this PVC resin show correlated D/a^2 values of 8×10^{-3} and 6.5×10^{-3} s⁻¹ at 70 and 100°C, respectively. The values obtained in this work are in good agreement with the prior correlated values.

The VCM contents measured after the fourth

strip include the effects of both the third strip and the fourth strip for the 50 and 70°C runs. For the 100°C run the VCM content was not changed by the fourth strip. Likewise, no significant change in VCM content was noted from the fourth to the fifth strip for the 50 and 70°C runs. The results of the fourth and fifth strips at 50 and 70°C and the results of the third and fourth strips at 100°C are taken as measures of the same residual VCM concentration.

A major uncertainty exists in any attempt to estimate diffusion coefficients and the activation energy for diffusion for 50 and 70°C for the lowest levels of VCM. For the 100°C strips it is clear that the minimum residual level is reached at the end of the third strip but this residual level may have been reached after the third strip or required some or all of the fourth strip to reach this residual level. Values of the diffusion coefficient estimated from the average of all VCM determinations and the assumption of 1 or 2 strips are as follows:

Stripping temp, °C	Value of D/a^2 , s ⁻¹	
	One strip required	Two strips required
50	1.86×10^{-3}	7.58×10^{-4}
70	6.79×10^{-3}	2.64×10^{-3}
100	5.76×10^{-3}	Not required

The values of D/a^2 are shown in Fig. 1. The values for the first strip fall very nearly on a straight line and yield a value for the activation energy of 18.2 Kcal. The values for the second strip show a break and yield 19.0 Kcal for the activation energy between 100 and 70°C and 29.0 Kcal for the activation energy between 70 and 50°C. Treatment of the data from the third and fourth strips can yield a range for the activation energy between 70 and 50°C. If it is assumed that one strip is required for both 50 and 70°C then the activation energy between 70 and 50°C is 14.3 Kcal while if it is assumed that one strip is required at 70°C and two are required at 50°C the activation energy is 24.2 Kcal. In both cases the activation energy for the 100-70°C temperature segment is 18.1 Kcal. These values are as follows:

Strip	Initial VCM, ppm	Activation energy, Kcal/g mole	
		100-70°C	70-50°C
1	0.7	18.2	18.2
2	0.023	19.0	29.0
3 and 4	0.0108	18.1	14.3-24.2

CONCLUSIONS FROM EXPERIMENTAL PROGRAM

• A non-migration level of 0.0006 to 0.001 ppm has been demonstrated for PVC resin that is used in bottle compound. This non-migration level appears to be independent of temperature in the range of 50 to 100°C.

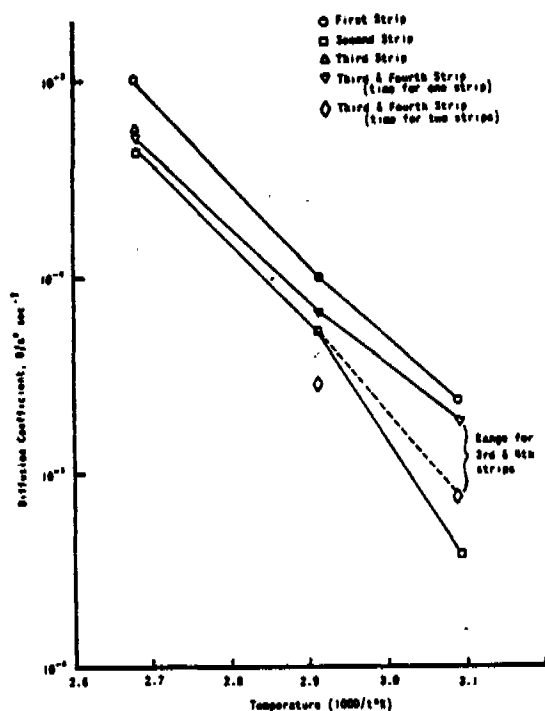


Fig. 1. Diffusion coefficients for VCM in PVC bottle resin.

• PVC bottles stored at 120°F with 50 percent aqueous ethanol as contents show a non-migration level of about 0.0008 ppm.

FUTURE WORK

We plan to repeat the second and third parts of the experimental program including GCMS analysis of the bottles after vegetable oil storage to separate VCM from interfering components. This is expected to explain the apparent increase in VCM that was shown with vegetable oil. Repetition of the experiments to obtain data for better definition of diffusion coefficients and activation energies can be accomplished by elimination of the drying problem that occurred with the work reported in this paper.

An experimental program shall also be carried out to determine the replicability of the analytical method for PVC bottles. The entire bottle wall from a bottle is required for a single analysis so replication data are not available for what is known to be a large, constant VCM composition sample. Similarly, variability in VCM concentration is not known for bottles in the same batch. This shall also be determined. This work is required because of the small differences in VCM concentration that are required with these experimental programs.

SUMMARY

Experimental data continue to show that there is a non-migration level of about one ppb for VCM in PVC bottle resin and in PVC bottles with food simulating solvents. With the possible requirement for a PVC compound at the non-migration level, we have produced a commercial quantity of compound in the one to two ppb VCM range to demonstrate capability of manufacture of this compound.

The Diffusion of Gases and Vapors in Rigid PVC

A. R. BERENS

The BFGoodrich Company
Research & Development Center
Brecksville, Ohio 44141

Gravimetric sorption rate measurements have been carried out for CO_2 , H_2O , and ten C₁-C₆ organic vapors at low concentrations ($\leq 0.2\%$) in PVC films and uniform-particle powders at 30°C. The dominant transport process in all cases appears to be Fickian diffusion. A distinguishable contribution of relaxation-controlled swelling was observed for the more soluble vapors, such as acetone and benzene. A significant contribution of surface adsorption to the total sorption process was detected only for the n-alkanes, among the penetrants studied. Diffusion coefficients, determined from half-sorption times and polymer dimensions, range from $4 \times 10^{-10} \text{ cm}^2/\text{sec}$ for H_2O to $1.5 \times 10^{-12} \text{ cm}^2/\text{sec}$ for n-hexane. Diffusivities determined in this study, in combination with those for gases reported by Tikhomorov, et al. (Makromol. Chem. 118 177 (1968)), define a continuous curve, covering more than nine orders of magnitude, when plotted as a function of the molar volume constant, b, of the van der Waals equation of state for gases and vapors.

INTRODUCTION

Current concern about possible environmental and physiological effects of minor, low-molecular-weight constituents of plastic materials has accentuated the importance of diffusion studies involving small molecules in glassy polymers. Knowledge of the diffusivity of small organic molecules in polymers is essential both for the design of processes for removing residual monomers or solvents and for the prediction of migration rates for remaining trace ingredients.

Until quite recently, studies of diffusion in glassy polymers have been largely limited to gaseous penetrants or to organic solvents at rather high concentrations. The diffusivities of a number of gases in unplasticized poly(vinyl chloride) (PVC), for example, were reported by Tikhomorov, et al. (1). For organic liquids or vapors at high relative pressures, sorption behavior in glassy polymers is quite complex; due to the superposition of diffusion and relaxation controlled swelling (2), the transport process cannot be described by simple Fickian diffusion equations. Hopfenberg and Frisch (3) suggested that simple Fickian diffusion is to be expected at very low penetrant activities or concentrations in glassy polymers; experimental studies under these conditions, however, have been hampered by the prohibitively long sorption times encountered with organic vapors in conventional polymer film specimens. Thus there has been a

notable lack of experimental data in the area of current concern, i.e., the diffusion of small organic molecules at low concentrations in rigid polymers.

In a recent study of the diffusion of vinyl chloride monomer (VCM) in PVC (4-6), gravimetric sorption measurements were performed with polymer powder samples of well-defined geometry. In powder samples, diffusion path lengths can be reduced by orders of magnitude below the practical limit of film thickness, and it is thus feasible to investigate diffusion processes which require inconveniently long times in films. At very low relative VCM pressure ($P_{rel} \leq \sim 0.01$, where $P_{rel} = P/P_0$, with P_0 the saturated vapor pressure), the sorption of VCM by PVC was found to follow simple Fickian kinetics; the diffusivity, D , was readily determined from the half-sorption time, $t_{0.5}$, and the powder particle diameter, d , as

$$D = 7.66 \times 10^{-3} \frac{d^2}{t_{0.5}} \quad (1)$$

At somewhat higher VCM pressure, the sorption process involved both Fickian diffusion and a slower, relaxation-controlled swelling; because of the rapid diffusion time in fine powders, it was still possible to estimate D from the early part of the sorption vs time curves (5).

The present study was undertaken in order to determine whether simple Fickian diffusion might generally be observed for low concentrations of

small organic molecules in unplasticized PVC. Gravimetric sorption experiments were performed using PVC powder samples with a range of vapors in an effort to relate diffusivity to the molecular size of the penetrant and thus to provide a basis for predicting migration rates of residuals from PVC and, perhaps, other rigid polymers.

EXPERIMENTAL

Materials

PVC homopolymer samples were prepared by emulsion and suspension polymerization techniques and were used in the powder form obtained directly from the polymerization by normal recovery and drying procedures. Particle structure was characterized by optical and electron microscopy and by nitrogen-adsorption surface area measurements. Samples of uniform particle diameter ranging from 0.11 to 0.44 μm were obtained by emulsion polymerization. The two suspension-type PVC samples consisted of ~ 100 μm agglomerates of 1.4 and 3.3 μm primary particles, respectively; in VCM sorption experiments, these samples followed uniform-sphere Fickian kinetics governed by the primary particle diameter (4). Some sorption-rate measurements were also made on a sample of rigid PVC film 50 μm in thickness. Research grade organic penetrants were employed throughout.

Equipment and Procedures

The time dependent weight changes of PVC samples upon exposure to penetrant vapors at predetermined pressures were determined using the Cahn electrobalance and vacuum system described previously (4). Most of the data reported here were obtained at 30°C in sorption experiments covering the vapor pressure interval from vacuum to $P_{\text{rel}} \leq 0.1$. The amount of vapor sorbed in each experiment was ≤ 4 mg per g PVC; the average penetrant concentration in the PVC during the experiment was thus ≤ 0.2 percent. For each vapor, sorption experiments were performed with PVC samples of several different particle sizes; experiments yielding half-sorption times ($t_{0.5}$) from 10 to 3600 s were included for calculations of diffusivities from Eq 1. With H_2O and CO_2 , $t_{0.5}$ for the largest-particle powder was too short to measure; diffusivities for these penetrants were obtained from sorption measurements on the 50 μm film sample, using the expression corresponding to Eq 1 for planar geometry,

$$D = 0.049 \frac{\ell^2}{t_{0.5}} \quad (2)$$

where ℓ is the film thickness (7).

RESULTS AND DISCUSSION

Sorption-Time Curves

For Fickian diffusion in a powder consisting of uniform spherical particles of diameter d , gravimetric sorption data obey the relation (4, 7)

$$M_t = M_\infty \left[1 - \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} \exp(-4Dn^2\pi^2 t/d^2) \right] \quad (3)$$

where M_t is the weight of penetrant sorbed at time t after an instantaneous change in pressure and M_∞ is the total sorbed at equilibrium. This expression predicts that a plot of M_t vs $t^{1/2}$ will be essentially linear until $M_t \approx 0.6 M_\infty$ and then will curve to approach M_∞ asymptotically. A curve of similar form is also predicted for Fickian sorption in a plane film of thickness ℓ (7):

$$M_t = M_\infty \left[1 - \frac{8}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{(2n+1)^2} \exp(-D(2n+1)^2\pi^2 t/\ell^2) \right] \quad (4)$$

For all of the sorption experiments reported here, plots of M_t vs $t^{1/2}$ are linear over a substantial portion of the total course of the experiment. This finding clearly indicates that the dominant transport process for all of the penetrants studied, at low concentrations in PVC, is simple Fickian diffusion.

For many of the experiments, the uniform-sphere Fickian diffusion model, Eq 2, accurately describes the gravimetric data throughout the sorption process. Examples of M_t vs $t^{1/2}$ plots obeying this relation are shown in Fig. 1, for the sorption of ethanol in the 0.44 μm PVC powder, and Fig. 2, for *n*-propanol in the 0.22 μm sample. Equation 4 similarly describes the sorption results on the film sample, as illustrated by the CO_2 sorption data plotted in Fig. 3.

In a number of cases, sorption experiments yielded M_t vs $t^{1/2}$ plots which are initially linear but do not approach equilibrium as promptly as predicted by Eq 2. This behavior is illustrated by the data for the sorption of acetone and benzene plotted in Figs. 4 and 5, respectively. The curves obtained by fitting Eq 3 to the initial portions of the experimental data are also shown in these figures. Sorption in excess of the Fickian curve may reasonably be attributed to relaxation-controlled swelling (5). The contribution of relaxation to the total sorption, in experiments covering a similar P_{rel} interval, seems greater for those penetrants having the higher solubility in PVC. For a given penetrant, the contribution of relaxation, relative to Fickian sorption, increases as the P_{rel} increment of the experiment is increased. In the experiments considered here, the combination of small P_{rel} intervals with small particle size (hence rapid dif-

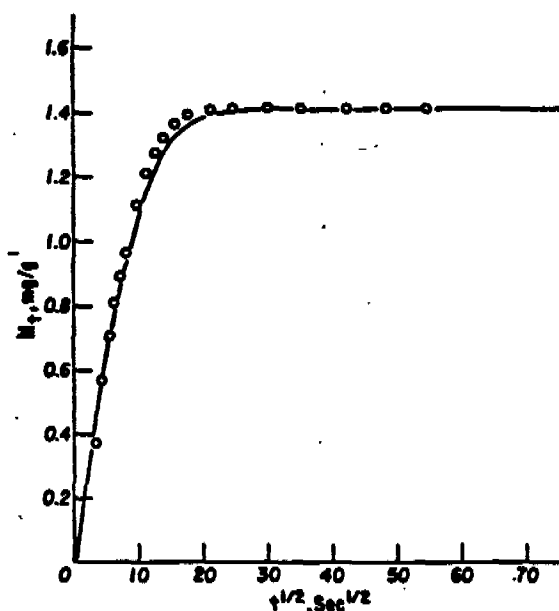


Fig. 1. M_t vs $t^{1/2}$ for sorption of ethanol in 0.44 μm PVC powder at 30°C. $P_{rel} = 0 \rightarrow 0.046$. Points, experimental; curve, Eq 3 with $M_\infty = 1.41$ mg/g, $D = 4.8 \times 10^{-12}$ cm²/s.

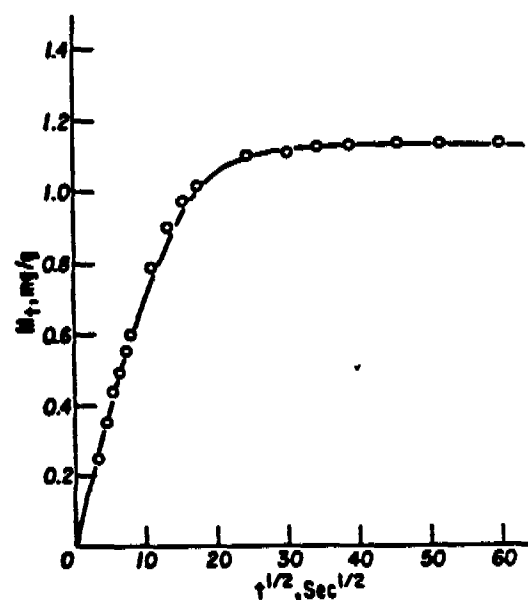


Fig. 2. M_t vs $t^{1/2}$ for sorption of n-propanol in 0.22 μm PVC powder at 30°C. $P_{rel} = 0 \rightarrow 0.108$. Points, experimental; curve, Eq 3 with $M_\infty = 1.13$ mg/g, $D = 6.7 \times 10^{-12}$ cm²/s.

Table 1. Summary of Diffusivity Measurements at 30°C

Penetrant	PVC sample	P_{rel} interval	Fickian sorption mg/g	$t_{0.5}$, s	D , cm ² /s	van der Waals b, liter/mol (9)
H ₂ O	50 μm film	0-.19	0.15	27	4.5×10^{-12}	0.0305
H ₂ O	50 μm film	.19-.41	0.60	36	3.4×10^{-12}	
CO ₂ (25°C)	50 μm film	0-.008	1.35	1470	8.4×10^{-18}	0.0427
Methanol	3.3 μm powder	0-.016	0.45	12	6.9×10^{-11}	0.0670
	3.3 μm powder	.018-.035	0.17	20	4.2×10^{-11}	
	3.3 μm powder	.035-.064	0.40	30	2.4×10^{-11}	
	1.4 μm powder	0-.100	1.3	12	1.3×10^{-11}	
VCM (ref. 4)					2.0×10^{-12}	0.080 (est)
Ethanol	0.44 μm powder	0-.39	7.3	45	3.3×10^{-12}	0.0641
	0.44 μm powder	0-.046	1.41	31	4.8×10^{-12}	
Acetone	0.44 μm powder	0-.010	3.2	106	1.4×10^{-12}	0.0994
n-Propanol	0.44 μm powder	0-.108	1.34	132	1.1×10^{-12}	0.1019
	0.22 μm powder	0-.108	1.13	55	6.7×10^{-12}	
	0.11 μm powder	0-.104	2.0	40	2.3×10^{-11}	
Benzene	0.22 μm powder	0-.059	10.4	210	1.8×10^{-11}	0.1154
n-Butane	0.44 μm powder	0-.037	0.88	780	1.9×10^{-11}	0.1226
	0.44 μm powder	0-.101	2.0	580	2.6×10^{-11}	
	0.22 μm powder	0-.011	0.77	156	2.4×10^{-11}	
n-Butanol	0.44 μm powder	0-.125	0.45	900	1.6×10^{-11}	0.138 (est)
	0.22 μm powder	0-.125	1.63	272	1.4×10^{-11}	
	0.11 μm powder	0-.120	2.54	90	1.0×10^{-11}	
n-Pentane	0.22 μm powder	0-.028	1.3	480	7.7×10^{-12}	0.1460
	0.22 μm powder	0-.102	3.0	200	1.8×10^{-11}	
	0.11 μm powder	0-.102	2.7	53	1.8×10^{-11}	
n-Hexane	0.22 μm powder	0-.103	> 4.0	~3600	1.0×10^{-12}	0.1735
	0.11 μm powder	0-.058	2.6	700	1.3×10^{-12}	
	0.11 μm powder	0-.109	3.0	400	2.3×10^{-12}	

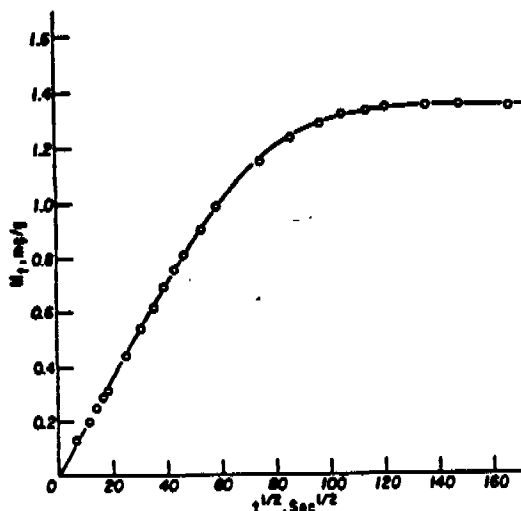


Fig. 3. M_t vs $t^{1/2}$ for sorption of CO_2 in 50 μm PVC film at 25°C, $P_{\text{rel}} = 0 \rightarrow 0.008$. Points, experimental; curve, Eq 4 with $M_\infty = 1.35 \text{ mg/g}$, $D = 8.4 \times 10^{-10} \text{ cm}^2/\text{s}$.

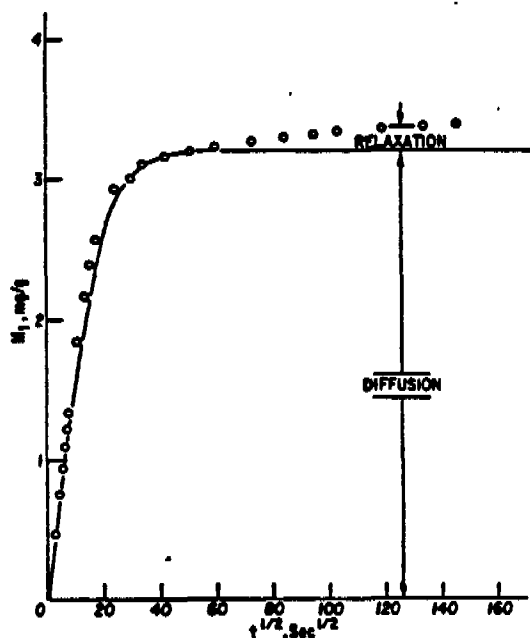


Fig. 4. M_t vs $t^{1/2}$ for sorption of acetone in 0.44 μm PVC powder at 30°C, $P_{\text{rel}} = 0 \rightarrow 0.0103$. Points, experimental; curve, Eq 3 with $M_\infty = 3.2 \text{ mg/g}$, $D = 1.4 \times 10^{-12} \text{ cm}^2/\text{s}$.

fusion equilibration) produces sorption curves which seem clearly separable into diffusion and relaxation contributions.

For n-butane, n-pentane, and n-hexane, the gravimetric sorption data show a nearly instantaneous initial weight gain, followed by sorption of the diffusion-plus-relaxation form observed with other penetrants. The M_t vs $t^{1/2}$ plots in Figs. 6 and 7

illustrate this behavior. The rapid initial weight gain increased with increasing molecular weight of the n-alkane, for a given P_{rel} interval and PVC particle size or surface area, and increased in approximate proportion to the specific surface area of the PVC powder sample, for a given penetrant and P_{rel} interval. This rapid weight gain, therefore, may reasonably be attributed to surface adsorption of the n-alkanes. Conversely, the absence of a de-

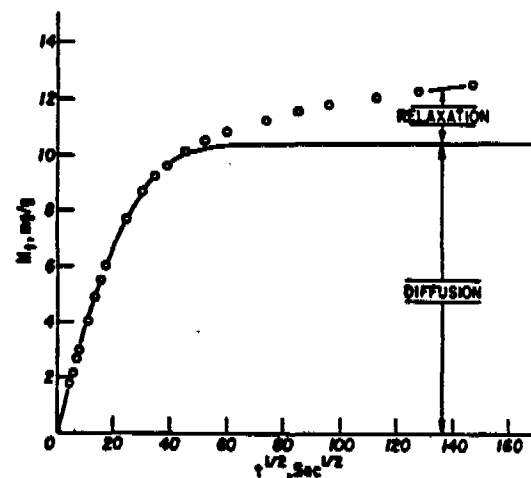


Fig. 5. M_t vs $t^{1/2}$ for sorption of benzene in 0.22 μm PVC powder at 30°C, $P_{\text{rel}} = 0 \rightarrow 0.059$. Points, experimental; curve, Eq 3 with $M_\infty = 10.4 \text{ mg/g}$, $D = 1.8 \times 10^{-12} \text{ cm}^2/\text{s}$.

tectable, nearly instantaneous weight gain for the other penetrants studied here indicates that surface adsorption was negligible in all other cases. The separate contributions of adsorption, diffusion, and relaxation processes to the total sorption may be estimated from the M_t vs $t^{1/2}$ curves as indicated in Figs. 6 and 7.

Diffusion Coefficients

For each of the penetrants studied, D has been calculated, through Eqs 1 or 2, from the half-sorption times, $t_{0.5}$, for the Fickian portion of the experimental sorption-time curves. The experiments and results are listed in Table 1. Where usable data were obtained on more than one PVC sample with a given penetrant, the agreement seems satisfactory. The diffusivities of H_2O and CO_2 agree quite well with those reported by Tikhomorov, *et al.* (1). For the organic vapors, D ranges from $\sim 4 \times 10^{-11} \text{ cm}^2/\text{s}$ for methanol to $\sim 10^{-13} \text{ cm}^2/\text{s}$ for n-hexane.

Correlation of D with Penetrant Size

The strong trend of decreasing diffusivity with increasing penetrant molecular weight suggests a correlation of D with the size of the penetrant

molecules. One measure of molecular size, available for most of the penetrants studied, is the constant b of the van der Waals equation of state (8)

$$\left(P + \frac{n^2 a}{V^2}\right)(V - nb) = nRT \quad (5)$$

Here, b is the effective volume of the molecules in one mol of gas, in liters/mol. Published values of b (9) for the penetrants studied are listed in Table I; interpolated estimates are given for vinyl chloride and *n*-butanol. In Fig. 8, diffusivities determined in this study are plotted against b ; a smooth correlation is seen to exist.

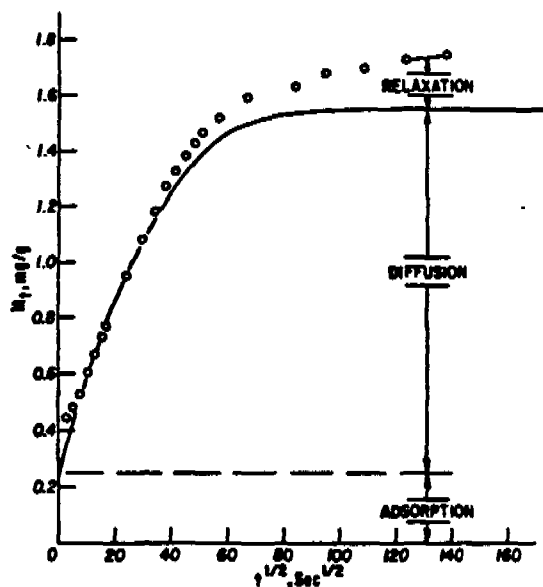


Fig. 6. M_t vs $t^{1/2}$ for sorption of *n*-pentane in 0.22 μ m PVC powder at 30°C, $P_{rel} = 0 \rightarrow 0.028$. Points, experimental; curve, Eq 3 with $M_\infty = 1.3$ mg/g, $D = 7.7 \times 10^{-10}$ cm²/s (adsorption, 0.25 mg/g).

Also plotted in Fig. 8 are the diffusivities of gases in PVC at 25° determined by Tikhomorov, *et al.* (1). Together, the two sets of data define a single smooth curve; only the points for the noble gases, neon, argon, and krypton, appear to lie significantly away from the curve. The combined data for gases and organic vapors thus show a continuous correlation with molecular volume extending over more than nine orders of magnitude of D , from 2.8×10^{-8} to $\sim 10^{-13}$ cm²/s.

This strong dependence of D upon penetrant size, for PVC below its T_g , contrasts markedly with the effect of penetrant size in rubbery polymers (10). For the same range of penetrant size, values of D in natural rubber at 40°C fall in the much narrower range of 10^{-5} to 10^{-6} cm²/s; D for C₄ to C₆ *n*-alkanes in polyisobutylene at 35° is essentially constant at $\sim 3 \times 10^{-9}$ cm²/s. Diffusion of small

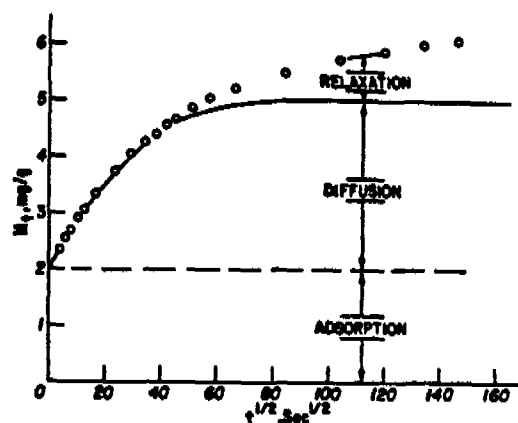


Fig. 7. M_t vs $t^{1/2}$ for sorption of *n*-hexane in 0.11 μ m PVC powder at 30°C, $P_{rel} = 0 \rightarrow 0.109$. Points, experimental; curve, Eq 3 with $M_\infty = 3.0$ mg/g, $D = 2.3 \times 10^{-10}$ cm²/s (adsorption, 2.0 mg/g).

molecules in rubbery polymers presumably involves cooperative motion of the penetrant and polymer chain segments of similar size; the narrow range of the observed diffusivities suggests that segmental motions involving from four to nine chain atoms occur at similar frequencies. In the glassy state, such segmental motion is effectively quenched, and diffusion probably occurs by jumps of penetrant molecules between sites or holes frozen into the polymer matrix. Diffusivity, then, may be a measure of the probability of finding holes large enough to hold a penetrant molecule. The very wide range of diffusivities found in this study seems to suggest that the probability of finding such holes is a continuous and sharply decreasing function of increasing hole size.

The very limited data available on diffusivity of organic vapors in other glassy polymers suggests that very low magnitudes of D are not unique to PVC. Ensore, *et al.* (11) have reported D of the order of 10^{-14} cm²/s for *n*-hexane in polystyrene at 30°C. Preliminary experiments in this laboratory on the sorption of acrylonitrile in styrene/acrylonitrile copolymer powders at 50°C indicate a D of approximately 4×10^{-11} cm²/s. Further application of the polymer powder/vapor sorption method may be expected to provide important information on the rate and mechanisms of small-molecular transport in a variety of glassy polymers.

Practical Implications

The results of this study seem to provide some useful generalizations in regard to the practical problems of removal and migration of low-molecular weight residuals from rigid plastic materials. The dominance of Fickian diffusion in governing the transport process at low penetrant concentrations, and the consequent dependence of diffusion time upon the square of particle diameter, suggest that polymers should be pro-

duced in the smallest feasible particle size, and that "stripping" should be performed while the polymer is in this form, in order to achieve most rapid and effective removal of residual monomers or solvents. On the other hand, the very low diffusivities of small organic molecules in glassy polymers indicates that migration of residuals from fabricated rigid plastic products will be extremely slow. Berens and Daniels (12) have applied Fickian diffusion equations to predict the rate of migration of residual monomer from PVC pipe, for example, and have shown that a pipe containing ≤ 1 ppm residual VCM will yield < 1 ppb VCM

strate that the transport of small molecules at low concentrations in rigid PVC is predominantly a Fickian diffusion process. The technique of gravimetric sorption using fine polymer powders is capable of determining diffusivities at least as low as 10^{-18} cm²/s. These experiments also can distinguish and quantify the individual contributions of surface adsorption, Fickian diffusion, and relaxation-controlled swelling to the total sorption process. Diffusivity values now available, determined at 25-30°C, span the range from 2.8×10^{-8} (helium) to 1.5×10^{-13} cm²/s (n-hexane). Over this entire range, diffusivity appears to be a smooth, continuous function of the molecular size of the penetrant, as measured by the molar volume term, b , of the van der Waals equation of state. This correlation seems quite relevant both to the basic understanding of transport processes in the glassy state and to the practical problems of removal and migration of residual monomers and solvents from rigid plastic materials.

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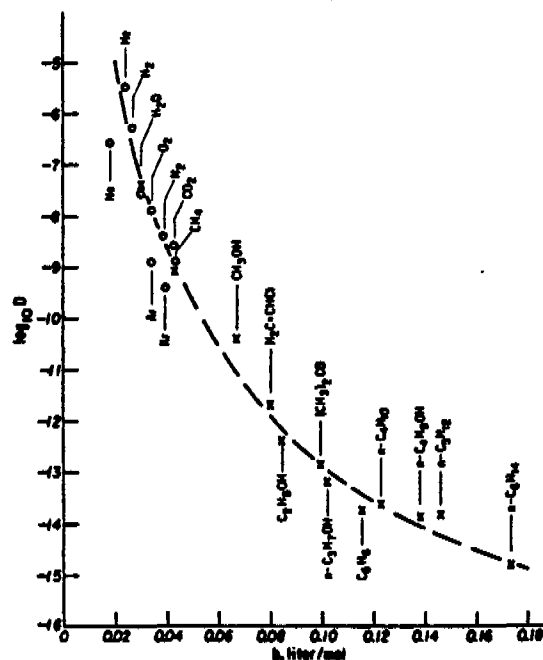


Fig. 8. Diffusivities of gases and vapors in PVC, plotted vs molar volume constant, b , of van der Waals equation of state a , ref. (1): X, this study.

in water contained in the pipe under any expected service conditions. The diffusivity data presented here may provide a reasonable basis for similar estimation of migration rates of other low molecular weight, minor constituents of rigid plastic products.

CONCLUSIONS

The results of this study, in conjunction with previous data for gaseous penetrants (1), demon-