

Sorption of Organic Liquids and Vapors by Rigid PVC

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Synopsis

The effects of activity and solvent strength of a number of organic penetrants upon their sorption kinetics and equilibria in poly(vinyl chloride) have been studied by gravimetric vapor and liquid sorption experiments at 30°C. For each solvent, the relation of equilibrium sorption to activity is well approximated by the Flory-Huggins equation with a characteristic value of the interaction parameter χ . The glass transition temperature T_g is depressed in direct proportion to the volume fraction of solvent absorbed; the composition corresponding to a T_g of 30°C, C_g (30°C), is in the range of 0.22–0.30 volume fraction for several common solvents. The form of the sorption kinetics varies with the ratio of the equilibrium sorption to C_g , and thus depends on the combined effects of χ , solvent activity, and plasticizing action. When the equilibrium sorption is less than about $C_g/2$, kinetics are Fickian, with the very low diffusivities typical of the glassy state; for sorption values between $C_g/2$ and C_g , anomalous kinetics are observed; and when the sorption is greater than C_g , transport in thin PVC films follows Case II kinetics. At high sorption levels, increasing film thickness produces a shift of the kinetics toward Fickian form with apparent diffusivity values typical of rubbery polymers.

INTRODUCTION

In practical service, rigid PVC pipes or containers may be exposed to a variety of organic liquids or vapors at concentrations ranging from pure compounds to trace environmental contaminants. Prediction of the behavior of the PVC product thus requires knowledge of the effects of both chemical nature and concentration on the rate and extent of sorption of the organic penetrant. In contact with straight liquids, for example, rigid PVC is quite resistant to alcohols and aliphatic hydrocarbons, swollen by aromatic and some halogenated hydrocarbons, and dissolved by certain esters and ketones.^{1–3} The immersion of PVC in liquid acetone was found to involve a Case II sorption process,⁴ but little else has been published regarding transport mechanisms in PVC at high penetrant activities. At low activities, organic vapors are sorbed into PVC according to Fickian kinetics, with very low diffusivities that depend only on the molecular size of the penetrant, and not on its chemical nature.⁵

The variation of transport mechanisms in glassy polymers with penetrant activity has been recognized for some time,⁶ but there have been few studies covering the entire activity scale. We recently undertook such a study to assess the possibility that rigid PVC water pipe might be permeated by organic soil pollutants, concluding that permeation would be negligible except in the case of a gross spill or leak of a strong swelling agent in the immediate vicinity of the pipe.⁷ Here we report some additional data from this recent

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study and discuss its relevance to the general question of transport kinetics in polymer/solvent systems.

EXPERIMENTAL

Because of the wide variation of sorption rates with penetrant activity, it is impractical to cover the whole activity range with a single type of polymer specimen. At low vapor activities, the time required to approach sorption equilibrium is prohibitively long even for the thinnest feasible film samples; measurements were therefore made on well-characterized PVC powders, for which the diffusion path is much shorter and the consequent sorption time much more accessible.⁵ For PVC powders in swelling solvents at high activities, on the other hand, sorption rates are immeasurably fast, and it is difficult to distinguish absorbed from entrapped solvent; PVC film or sheet specimens were therefore used in the high activity range, and sorption rates were determined during immersion in pure or mixed liquids. Gravimetric methods were used in both vapor and liquid sorptions, and all experiments were carried out at 30°C.

Materials. The PVC powder samples were an experimental monodisperse emulsion polymer of 0.4- μm particle diameter, and a commercial suspension resin (Geon 103EP, The B. F. Goodrich Co.) of 2- μm average primary particle size. Film samples were prepared by mill-mixing suspension PVC with 2 wt % tin stabilizer, then extruding or compression molding to thicknesses from 0.06 to 4.2 mm. Organic solvents were Certified A.C.S. grade; the poly(ethylene glycol) (PEG 400) was Union Carbide's Carbowax 400.

Vapor Sorption Experiments. Gravimetric vapor uptake data were obtained as a function of time with a Cahn 2000 recording Electrobalance in a vacuum system thermostatted at 30°C and equipped with a pressure transducer/controller to hold vapor pressure P constant to within 0.2 mm Hg. Sorption runs of up to 10 days duration were made with acetone, benzene, and toluene at activities up to 0.75. (Activity = P/P_0 , where P_0 is the saturated vapor pressure at the experimental temperature.) Chlorinated solvents were not used in the Cahn balance because of their possible decomposition and attack on the aluminum balance components and sample pan.

Liquid Immersion Experiments. Sorption rate data for PVC sheet samples immersed in organic liquids at 30°C were obtained by periodically removing the samples, quickly blotting to remove free liquid from their surface, weighing on a fast-response electronic analytical balance (Mettler Model AE163), and then re-immersing. Measurements were made with about 20 pure liquids (activity = 1), including a number of chlorinated and aromatic hydrocarbons. Liquid sorption data at reduced penetrant activity were obtained by using solutions of PEG 400 in the relevant solvent; this solute serves as an inert activity depressant, and its absorption by PVC is negligible because of its high molecular weight and low affinity for the polymer. Since the vapor pressure of PEG 400 is much lower than that of the solvents, penetrant activities were approximately equal to P_t/P_0 , where P_t is the equilibrium vapor pressure of the solvent/PEG 400 mixture.

Depression of T_g . Glass transition temperatures T_g of PVC containing varied concentrations of swelling agents were measured by differential scan-

ning calorimetry (Perkin-Elmer DSC-2) on sheet samples equilibrated with solvent/PEG mixtures at several activities.

RESULTS AND DISCUSSION

Sorption Isotherms. For several of the solvents used here, the isotherms relating equilibrium solubility in PVC at 30°C to solvent activity, P/P_0 , have been established by combining vapor sorption data for PVC powders with liquid sorption data for PVC sheet samples. As an example, the combined equilibrium solubility data for toluene are shown in Figure 1 as a plot of percent weight gain vs. toluene activity. The percent weight gain, $W\%$, is related to the volume fractions of solvent and polymer, V_1 and V_2 , respectively, by

$$W\% = 100(V_1/d_1/V_2d_2) \quad (1)$$

where d_1 and d_2 are the solvent and polymer densities. Data from vapor and liquid sorptions on various PVC samples are in satisfactory agreement and lie close to a smooth curve over the whole activity range. As also shown in Figure 1, this isotherm is adequately described by the Flory-Huggins equation,⁸

$$\ln(P/P_0) = \ln(V_1) + V_2 + \chi(V_2)^2 \quad (2)$$

with the interaction parameter $\chi = 0.75$. This value properly characterizes toluene as a moderately strong swelling agent, since true solvents for a polymer have $\chi \leq 0.5$, and nonswelling nonsolvents have $\chi > 1$.

Solubilities in PVC as functions of solvent activity have also been determined from vapor and liquid sorption data for benzene, acetone, ethylene

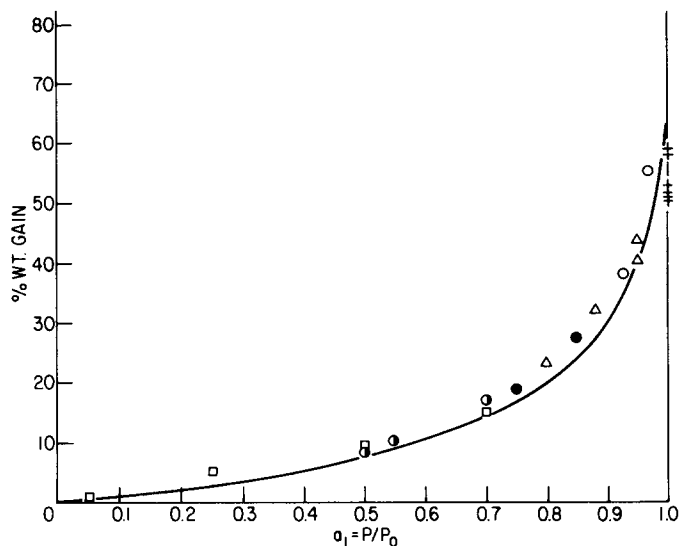


Fig. 1. Equilibrium sorption of toluene by PVC vs. toluene activity. Curve is Flory-Huggins equation with $\chi = 0.75$. (+) liquid C_6H_6 , 25-75 mil sheet; (●) vapor with 103EP powder; (○) vapor with 4 mil film; (○, △) C_6H_6 /PEG 400 liq./25 and 5.11 mil sheets, respectively; (□) vapor, 0.4 μm powder.

TABLE I
 Equilibrium Swelling and Interaction Parameters for PVC/Organic Solvent Systems

| Compound | Equilibrium sorption | | Time ^a (h) | Interaction parameter χ |
|---|----------------------|--------------|--------------------------|---------------------------------|
| | % Wt gain | Vol fraction | | |
| CH ₂ Cl ₂ | > 800 (sol) | > 0.89 | 2 | < 0.53 |
| CHCl ₃ | 227 | 0.68 | 6 | 0.64 |
| CCl ₄ | ~ 0 | ~ 0 | (280) | — |
| 1,1-C ₂ H ₄ Cl ₂ | 132 | 0.61 | 6 | 0.68 |
| 1,2-C ₂ H ₄ Cl ₂ (EDC) | ~ 700 (sol) | > 0.86 | 6 | < 0.55 |
| 1,1,1-C ₂ H ₃ Cl ₃ (TCA) | 67 | 0.42 | 600 | 0.85 |
| 1,1,2-C ₂ H ₃ Cl ₃ | > 400 (sol) | > 0.80 | 10 | < 0.56 |
| C ₂ HCl ₃ (TCE) | 70 | 0.40 | 5 | 0.88 |
| C ₂ Cl ₄ | 35 | 0.23 | 800 | 1.17 |
| 1,2-C ₃ H ₆ Cl ₂ | 176 | 0.68 | 20 | 0.68 |
| Benzene | 50 | 0.44 | 12 | 0.83 |
| Toluene | 50–60 | 0.45–0.49 | 15 | ~ 0.80 |
| Xylene | 42 | 0.40 | 100 | 0.88 |
| Acetone | 170 | 0.75 | 2 | 0.61 |
| Methanol | ~ 1 | — | (300) | — |
| Ethanol | ~ 0.1 | — | (300) | — |
| Isopropanol | ~ 0.5 | — | (300) | — |
| <i>n</i> -Hexane | ~ 0.6 | — | (160) | — |
| Vinyl chloride ¹⁴ | 30 | 0.33 | — | 0.98 |

^aTime to apparent equilibrium in 0.6 mm PVC or (duration of experiment).

dichloride, and trichloroethylene. In each case, when χ is adjusted to fit the solubility of the pure liquid ($P/P_0 = 1$), data over the whole activity range are well described by eq. (2). These results suggest that the Flory–Huggins equation, with interaction parameters determined from equilibrium sorption of the pure liquids, can provide useful estimates of sorption isotherms for other solvents, as well.

Table I lists the equilibrium solubilities of the above solvents and several other pure organic liquids in PVC at 30°C and the values of χ estimated through eq. (2) from V_1 at $P/P_0 = 1$. The aromatic hydrocarbons and most of the chlorinated solvents tested are swelling agents or marginal solvents for PVC, having χ values in the range 0.5–1.0. Hexane, carbon tetrachloride, and the alcohols were absorbed to less than 1 wt %, in immersions of at least 1 week, and presumably have $\chi > 1.0$.

Plasticization by Solvents. The degree of plasticization of PVC may be expressed as the depression of the glass transition temperature T_g . Values of T_g determined by DSC on solvent-swollen PVC sheet samples are shown in Figure 2 as a function of solvent volume fraction V_2 . The experimental results closely follow linear correlations between volume fraction composition and the T_g 's of the individual components,

$$T_g = V_1 T_{g1} + V_2 T_{g2} \quad (3)$$

with $T_{g2}(\text{PVC}) = 358 \text{ K}$ and T_{g1} taken as $0.63 T_{m1}$, where T_{m1} is the melting point of the solvent.⁹ The penetrant concentration C_g (in volume fraction units) which lowers the glass temperature to T_g can therefore be estimated

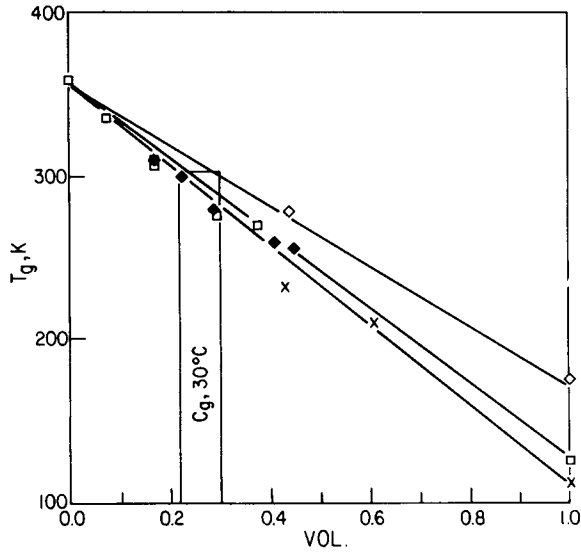


Fig. 2. Glass transition temperatures of solvent-swollen PVC vs. volume fraction solvent: (□) TCE; (◆) toluene; (×) acetone; (◇) benzene.

from the known melting points of the solvents. From (3) it follows that

$$C_g = (T_{g2} - T_g) / (T_{g2} - 0.63T_{m1}) \tag{4}$$

The melting points of the solvents studied here fall in the range from 178 K (acetone, toluene) to 278 K (benzene). For $T_g = 303$ K, the temperature of our sorption studies, eq. (4) yields C_g values in the range $0.22 < C_g < 0.30$. This calculation indicates that when the solvent uptake exceeds this range, the swollen PVC will have a T_g below 30°C , i.e., the PVC/polymer phase will be plasticized to the rubbery state under the experimental conditions.

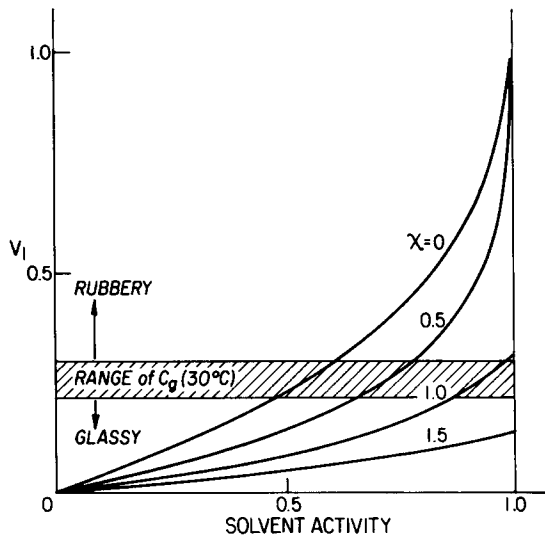


Fig. 3. Relation of glass transition composition C_g to Flory-Huggins isotherms for varied χ .

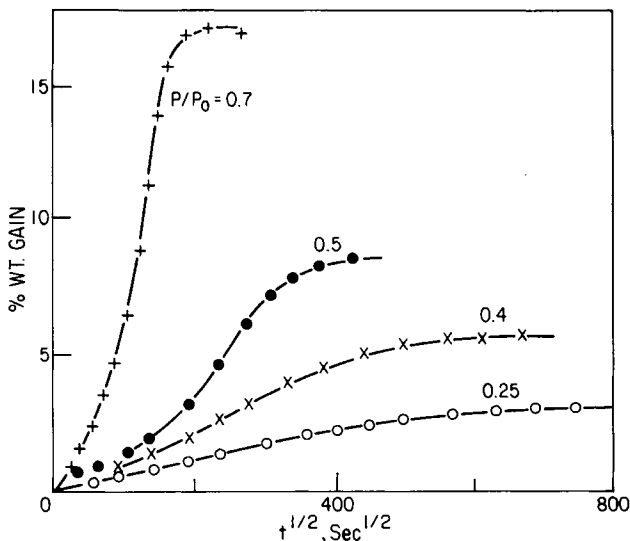


Fig. 4. Weight gain vs. $t^{1/2}$ for sorption of toluene vapor by 2- μ m PVC powder, at varied toluene activity.

The effects of solvent activity and χ upon plasticization may be illustrated by Figure 3, where the range of $C_g(30^\circ\text{C})$ is superposed on a set of Flory-Huggins isotherms for several arbitrary χ values. This figure implies that the PVC/solvent system remains in the glassy state so long as the isotherm remains below the transition region at C_g , and becomes rubbery when either higher activity or greater polymer/solvent interaction (lower χ) produces sorption greater than C_g . Thus PVC will be plasticized into the rubbery state at unit solvent activity and 30°C only by solvents whose χ is about 1.0 or less. Even a good solvent for PVC ($\chi = 0$) will produce the rubbery state only at activities > 0.5 . For swelling agents with χ in the range 0.5–1.0, plasticization to the rubbery state would require activities of about 0.75 or greater.

In Figure 3, representation of the sorption isotherms below C_g as curves of the Flory-Huggins form is intended as an approximation only, since isotherms for glassy PVC generally show a concave-downward, "dual-mode" form.¹⁰ The Langmuirian contribution disappears at the glass transition, however, and does not alter the general relations between activity, χ , and plasticization.

Vapor Sorption Kinetics—Toluene. Sorption experiments have been carried out on several PVC powder and film samples in toluene vapor at activities from 0.05 to 0.75. Kinetic data on a commercial suspension resin of 2- μ m average primary particle size at several toluene activities are shown in Figure 4 as plots of % weight gain vs. square root of sorption time. At activity 0.25, the data are of classic Fickian form—linear with $t^{1/2}$ for about the first half of the uptake, then asymptotically approaching equilibrium. From the initial slope and the particle diameter, the diffusivity D was estimated as 10^{-14} cm^2/s , a value quite reasonable for such a vapor in glassy PVC at low activity.⁵ At 0.4 activity, and more markedly at 0.5 and 0.7, the sorption vs. $t^{1/2}$ curves show a non-Fickian upward curvature and a greatly increased rate. Non-Fickian behavior at $P/P_0 \geq 0.5$ was also evidenced by the crossover of

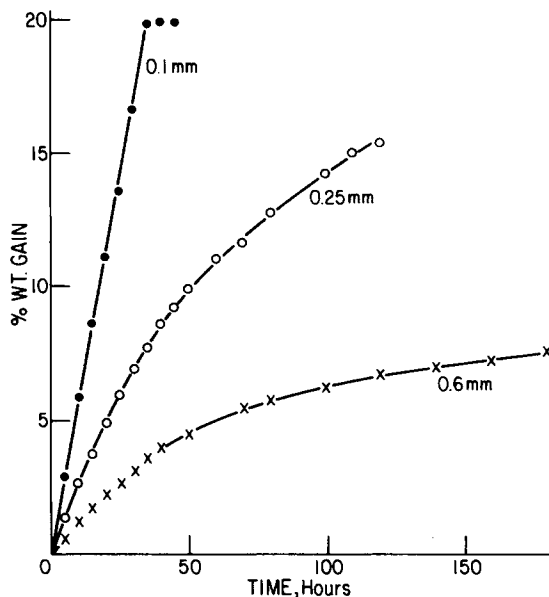


Fig. 5. Weight gain vs. time for sorption of toluene vapor at $P/P_0 = 0.75$ by PVC films of varied thickness.

conjugate sorption and desorption curves¹¹; the desorption curve is initially steeper, and then crosses the sorption curve and approaches its limit much more slowly.

For a $0.4\text{-}\mu\text{m}$ PVC powder and for a $60\text{-}\mu\text{m}$ PVC film, sorption of toluene vapor at 0.25 activity also showed Fickian kinetics, and D agreed very well with the value for the $2\text{-}\mu\text{m}$ powder. These samples, too, showed increasing deviations from Fickian behavior at toluene activities above 0.4. At $P/P_0 = 0.75$, sorption in the $60\text{-}\mu\text{m}$ film closely followed Case II kinetics, with uptake directly proportional to time. However, in contrast to the dimension-independent Fickian behavior at 0.25 activity, there is a pronounced variation in kinetics with sample dimensions at $P/P_0 = 0.75$: As shown in Figure 5, the uptake vs. time curves shift from linear, Case II form for the thinnest film toward Fickian behavior with increasing film thickness.

It seems possible to relate the effect of toluene activity on the sorption kinetics to the degree of plasticization produced by varying concentrations of absorbed toluene. The change from Fickian to anomalous behavior occurs near 0.5 activity, where the equilibrium toluene sorption is about 10 wt %, or 0.14 volume fraction; this is about half of the glass transition concentration $C_g(30^\circ\text{C})$. The sorption process at this activity thus involves appreciable swelling of the polymer, but the swollen polymer remains in the glassy state. At 0.75 activity, where sorption kinetics in a thin film become Case II, the equilibrium toluene volume fraction is 0.25, very close to C_g . The onset of Case II behavior thus seems to correspond to the glass-to-rubber transition.

Sorption Kinetics, Other Vapors. Sorption of benzene vapor at several activities in the $2\text{-}\mu\text{m}$ suspension PVC powder followed the same kinetic pattern as toluene: Fickian behavior at 0.25 activity, and faster, increasingly non-Fickian kinetics at 0.5 and 0.75 activity. The apparent diffusivities and

equilibrium uptakes of benzene were also similar to the toluene results, as might be expected from the chemical and geometrical similarity of these molecules. For acetone vapor in the same PVC powder, sorption appeared Fickian at 0.2 activity, but was already noticeably non-Fickian at $P/P_0 = 0.3$ and extremely so at 0.5. The sorption rate and equilibrium uptake of acetone are significantly higher than for toluene or benzene at similar activities, reflecting both the smaller molecular size and the stronger affinity (lower χ) of acetone for PVC. Thus the onset of non-Fickian behavior occurs at similar penetrant concentrations, and therefore similar degrees of plasticization, rather than similar activity, for these three penetrants.

Liquid Sorption Kinetics. The effects of penetrant activity upon kinetics of sorption into 0.3 mm PVC sheet from a liquid phase have been studied for several organic solvents. Mixtures with varied amounts of PEG 400 were used to cover the activity range from 0.6 to 1.0. Results for toluene, trichloroethylene (TCE), and ethylene dichloride (EDC), indicated that PEG behaved as the desired inert, nonsorbing activity depressant. For acetone, a stronger swelling agent, however, a discrepancy between weights gained in liquid and vapor sorption at the same activity indicated the sorption of a small amount of PEG from the liquid phase.

Liquid sorption data for toluene⁷ show a strong decrease in both rate and equilibrium uptake as the penetrant activity is reduced from 1.0 to 0.6. The form of the kinetics, however, remains Case II over this range, with uptake

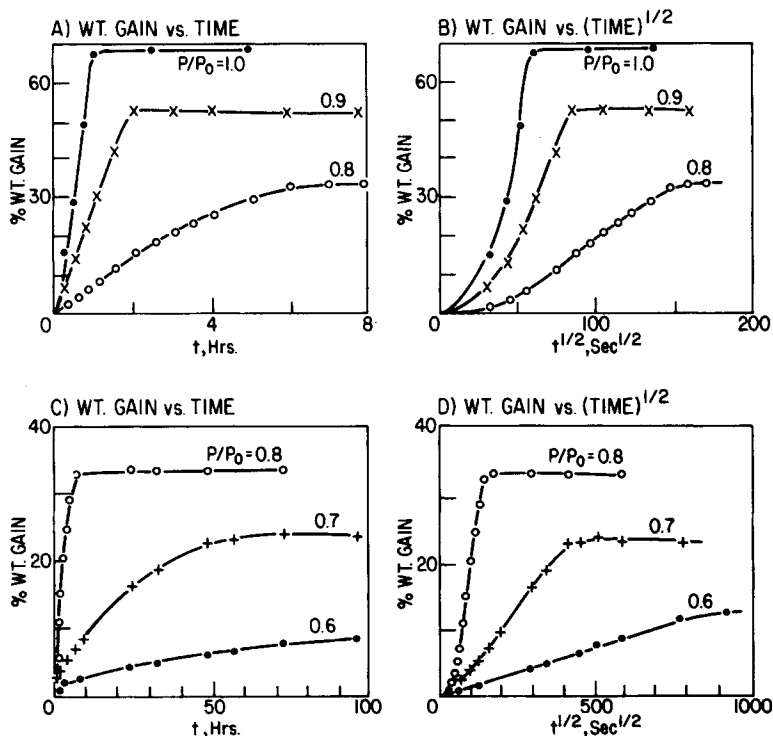


Fig. 6. Weight gain vs. t and vs. $t^{1/2}$ for sorption of TCE by 0.3 mm PVC films from liquid TCE/PEG 400 mixtures of varied TCE activity.

proportional to time. In the toluene activity range 0.6–0.75, where both liquid and vapor sorption data were obtained, results of the two techniques were in satisfactory agreement.

In the case of TCE, the kinetic form, as well as the rate and amount of sorption, shows a significant change over the activity range from 0.6 to 1.0. In Figure 6, sorption data for 0.3 mm PVC sheet at several TCE activities are plotted both against t and against $t^{1/2}$; different scales are used to cover the wide variations in rate and equilibrium sorption. The uptake vs. t plots show exemplary Case II, linear form at $P/P_0 = 1.0$ and 0.9, but curve downward at lower activity, tending toward Fickian behavior. The linear $t^{1/2}$ plot at 0.6 activity defines the upper end of the activity range for Fickian behavior of TCE. At this activity, the equilibrium sorption of TCE is about 12%, corresponding to a volume fraction $V_1 = 0.10$. At $P/P_0 = 0.7$, the equilibrium weight gain is 24 wt %, or $V_1 = 0.19$, and the sorption vs. $t^{1/2}$ plot shows a distinct upward curvature. Thus the onset of non-Fickian kinetics occurs at a TCE volume fraction near 0.15, or approximately $C_g/2$. At a TCE activity of 0.9, where sorption kinetics becomes Case II, the equilibrium weight gain is 52%, and $V_1 = 0.33$, or approximately C_g . Thus the changes in form of the sorption kinetics, from Fickian to anomalous and to Case II, occur at roughly the same ratios of equilibrium sorption to C_g for TCE as for toluene, although the penetrant activities at the transitions are quite different.

For EDC, a stronger swelling agent than TCE, Case II sorption was observed at $P/P_0 = 1.0$ ($V_1 > 0.85$) and at $P/P_0 = 0.9$ ($V_1 = 0.45$, still well above C_g). Again, there was a shift toward Fickian kinetics at lower activity, but the concentrations at the transitions from Case II to anomalous to Fickian behavior could not be closely defined from the available data.

Effect of Sample Thickness on Sorption Kinetics. A dependence of the form of sorption kinetics upon sample dimensions, as noted in our toluene vapor sorption experiments (Fig. 5), has been recognized for many years.¹² We have further studied this effect by liquid immersion experiments with toluene and TCE at activities ≥ 0.8 . The observed effects were similar for these two penetrants, and are here illustrated by data obtained for sorption of straight liquid TCE by PVC sheet samples of 0.25–4.2 mm thickness. Figure 7 shows weight gain data plotted both vs. t and vs. $t^{1/2}$. The equilibrium sorption is unaffected by film thickness, but the apparent kinetics change from Case II (linear with t) for the thinnest film to Fickian (linear with $t^{1/2}$) for the thickest. The apparent diffusivity of TCE, calculated from the slope of the $t^{1/2}$ plot for the 4.2 mm sheet, is 1.7×10^{-7} cm²/s; this value is many orders of magnitude higher than would be expected in glassy PVC, but is reasonable for Fickian diffusion of TCE in a soft, *rubbery* polymer. One might therefore infer that the rate-controlling step in TCE sorption into thick PVC samples may be Fickian diffusion through the swollen, rubbery surface layer.

Further support for a surface-layer controlled mechanism is provided by examining the data in several other ways. In Figure 8, the data of Figure 7 are replotted as M_t/M_∞ , the fraction of equilibrium sorption, vs. $t^{1/2}/h$, where h is sample thickness; these coordinates result in superposition of data for various h when diffusion is Fickian. On this normalized time scale, early time sorption of TCE for the thinner PVC films appears relatively slower, but then the slope becomes nearly parallel to that for the thicker samples. It appears

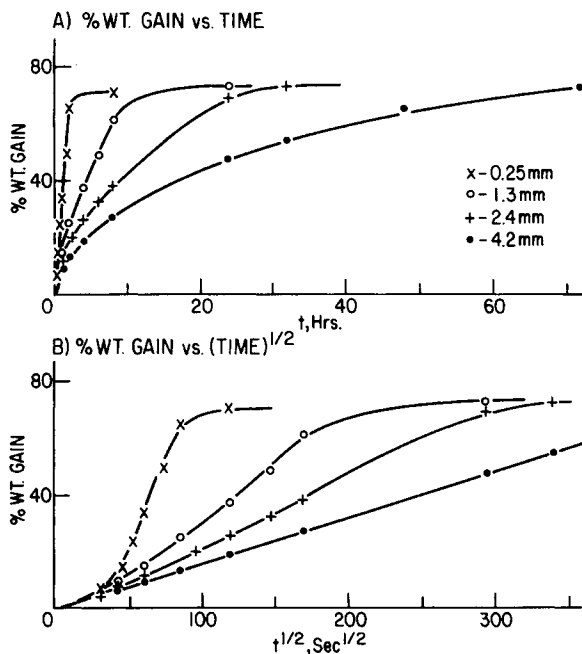


Fig. 7. Weight gain vs. t and vs. $t^{1/2}$ for sorption of liquid TCE by PVC sheets of varied thicknesses (mm): (x) 0.25; (o) 1.3; (+) 2.4; (●) 4.2.

that a similar "Fickian" rate is approached for films of differing thickness after an acceleration stage which is shorter, relative to the total sorption time, for films of greater thickness. In Figure 9, the same data are plotted as weight gain per unit initial surface area vs. $t^{1/2}$. Here, sorption follows a common curve for time periods that increase with sample thickness, and then rather abruptly ceases. This behavior suggests that a sharp concentration profile progresses into the sample until the unswollen core disappears.

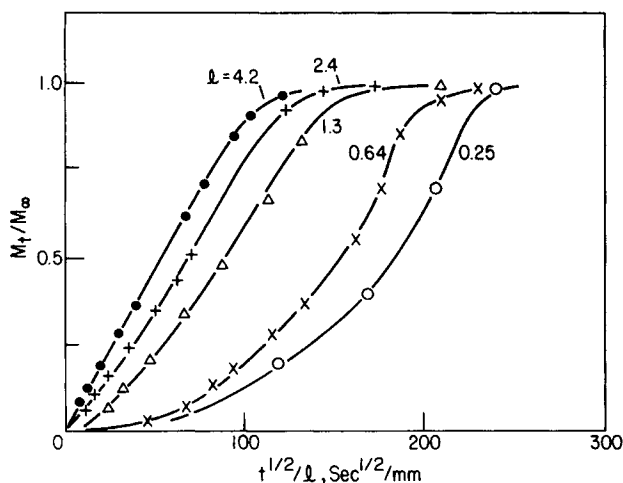


Fig. 8. Data from Figure 7 replotted as M_t/M_∞ vs. $t^{1/2}/h$.

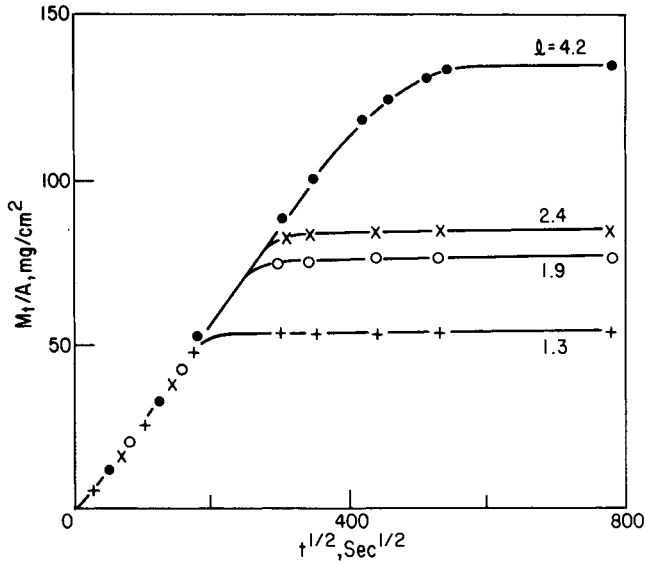


Fig. 9. Data from Figure 7 replotted as weight gain per unit surface area vs. $t^{1/2}$.

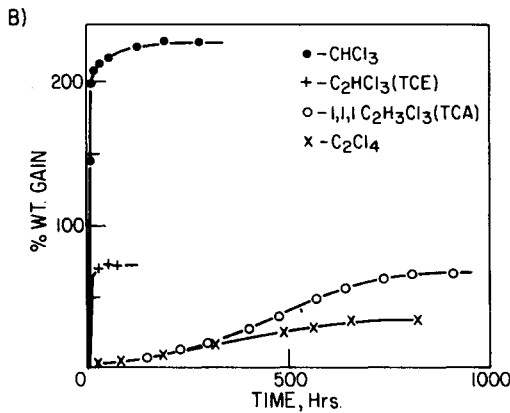
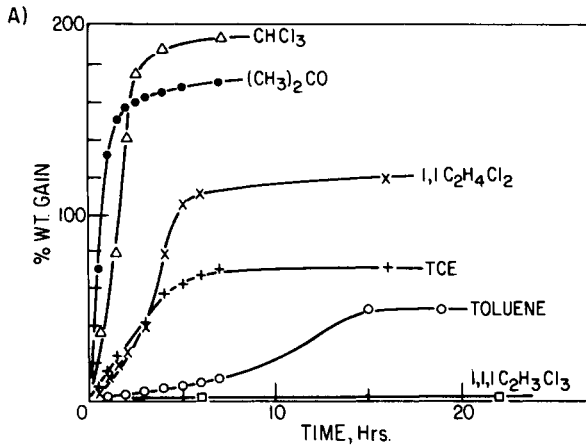


Fig. 10. Weight gain vs. time for 0.6 mm. PVC film in various organic liquids: (●) CHCl_3 ; (+) C_2HCl_3 (TCE); (○) $1,1,1\text{-C}_2\text{H}_3\text{Cl}_3$ (TCA); (×) C_2Cl_4 .

These observations all seem consistent with a "moving front" sorption process in which the rate-controlling factor changes with depth of penetration. Initially, the front advances at a constant rate (Case II kinetics) controlled by relaxation at the front. For thin films, the glassy core disappears and sorption ceases while this is still the controlling factor. During sorption in thicker sheets, however, the swollen surface layer becomes thick enough that penetrant diffusion through this rubbery phase limits the supply of penetrant to the front. Then, although the mechanism still involves a sharp concentration front, the kinetic form becomes Fickian, with an apparent diffusivity characteristic of a rubbery polymer. In support of this mechanism, we have observed, under an optical microscope, a sharp boundary advancing in proportion to $t^{1/2}$ in thick PVC samples immersed in toluene. Similar observations have been reported for PVC in a number of other strongly swelling solvents.¹³

Other Penetrants. Less extensive sorption rate measurements have been made for PVC in the other organic liquids listed in Table I. Uptake vs. time curves for 0.6 mm PVC films in several solvents at unit activity are shown in Figure 10. The rate of sorption generally increases with increasing equilibrium uptake and solvent strength, i.e., with decreasing χ . Molecular size and shape of the penetrant seem also to have a substantial effect, as illustrated by comparison of TCE and 1,1,1-trichloroethane (TCA): These two solvents have similar χ values, but TCE reaches sorption equilibrium in 0.6 mm PVC in about 6 h, while TCA requires about 800 h to reach a similar equilibrium uptake. By analogy with molecular shape effects on diffusivity of organic vapors in glassy PVC,⁵ the low rate of sorption of TCA may be attributed to the bulky, globular shape of this molecule.

CONCLUSIONS

The major factors affecting the sorption kinetics of low-molecular-weight organic compounds in rigid PVC at 30°C are the solvent power of the penetrant, measured by its polymer solvent interaction parameter χ , and the penetrant activity, or partial pressure, to which the PVC is exposed. These two factors govern the equilibrium penetrant concentration in the PVC, which in turn determines the degree of plasticization. Plasticizing effectiveness is similar for a number of common solvents: $C_g(30^\circ\text{C})$, the concentration which depresses the T_g of PVC to 30°C, is in the range of 0.22–0.30 volume fraction solvent. When the equilibrium sorption is less than about $C_g/2$, sorption is Fickian and relatively slow. Faster, non-Fickian or "anomalous" sorption is observed for equilibrium uptakes from about $C_g/2$ to C_g . For higher extents of sorption, i.e., when the swollen PVC is in the rubbery state, Case II sorption kinetics are observed for thin PVC films. At high sorption levels in thicker samples, sorption kinetics become apparently Fickian, with diffusivities typical of a rubbery polymer. The transport process then involves a sharp concentration front advancing in proportion to the square root of time, as diffusion through the swollen surface layer becomes the governing kinetic factor.

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