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Gravimetric and Volumetric Study of the Sorption of Gases and Vapors in Poly(Vinyl Chloride) Powders

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The sorption of a variety of gases and organic vapors in poly(vinyl chloride) (PVC) powders has been studied gravimetrically with a recording microbalance and volumetrically with a gas pycnometer and an automatic surface area analyzer. For nitrogen, carbon dioxide, vinyl chloride, methanol, acetone, n-butane, and benzene at low penetrant activities and temperatures below T_g, sorption isotherms exhibit the downward curvature characteristic of dual-mode sorption. The solubility of each of these penetrants is lower in heat-treated PVC samples than in samples recovered from the polymerization without additional heating. It has been possible to estimate the parameters of the dual-mode sorption model for carbon dioxide, vinyl chloride, and methanol. The results indicate that the history-dependence of gas or vapor solubility is associated only with the "hole-filling" term of the dual-mode model; the normal dissolution or Henry's Law term is essentially unaffected by the prior heat treatment of the PVC.

INTRODUCTION

Previous study of the sorption of vinyl chloride monomer vapor (VCM) in PVC resin powders (1) has delineated the behavior of this system with variations of temperature and vapor activity. Above the glass transition temperature (T_g = ~85°C), the Flory-Huggins equation describes the sorption isotherms over the full range of vapor activity. At low VCM activities below T_g, the isotherms show a pronounced downward curvature, which was interpreted in terms of the dual-mode sorption theory (2). The total sorption of VCM was ascribed to contributions of Flory-Huggins dissolution and Langmuirian "hole-filling", as shown in *Fig. 1*. The disappearance of the hole-filling contribution with increasing VCM pressure below 85°C was attributed to plasticization of the PVC by sorbed monomer. Values of T_g, as a function of VCM concentration in PVC, have been obtained by a thermomechanical method (3) and from the temperature-dependence of the limiting conversion of VCM polymerization (4). The temperatures and compositions at which the experimental sorption isotherms join the Flory-Huggins curve (see *Fig. 1*) correspond very well to the T_g vs composition data, as shown in *Fig. 2*. Dual-mode sorption in the VCM/PVC system thus appears characteristic of the glassy state while simple Flory-Huggins behavior occurs in the rubbery region of composition and temperature.

In the glassy state, the apparent equilibrium solubility of VCM in PVC was found to vary with the post-polymerization thermal history of the polymer sample (5). It was suggested that the content of holes or microvoids in the PVC sample is determined by the conditions prevailing when the sample was brought from the rubbery to the glassy state, and that the microvoid content, in turn, determines the extent of Langmuirian sorption in subsequent exposure to VCM vapor. Variations in post-polymerization history are illustrated on plot of T_g vs composition in *Fig. 3*. At the

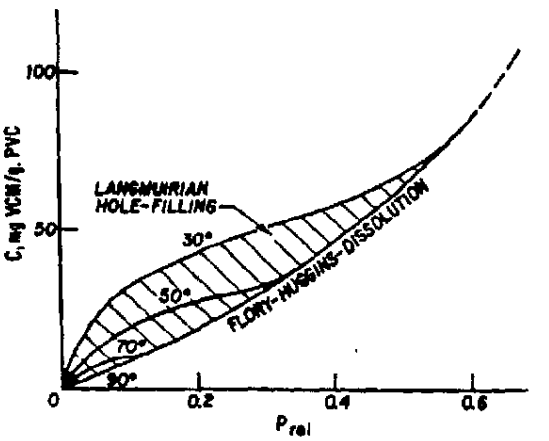

Fig. 1. Sorption isotherms for vinyl chloride in PVC, from Ref. (1).

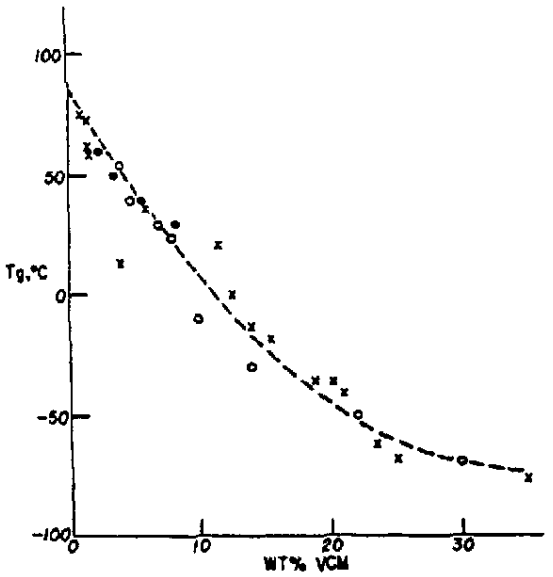

Fig. 2. T_g vs composition, VCM/PVC. X, thermomechanical data (4); ○, limiting conversion (4); ●, disappearance of hole-filling sorption.

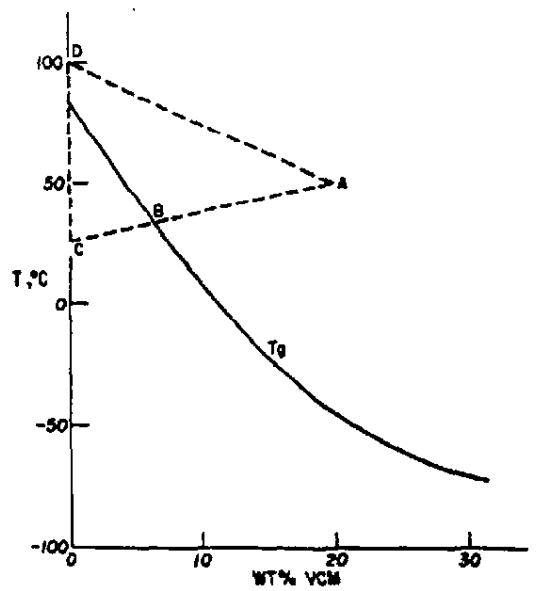

Fig. 3. Post-polymerization thermal history variations of PVC samples. ABC, "never-heated"; ADC or ABCDC, heat-treated.

end of a typical polymerization (50°C, 80 percent conversion), the PVC/VCM system is in the rubbery state. Removal of residual monomer without raising the temperature brings the polymer into the glassy state while it is still swollen with monomer (*Fig. 3*, path ABC). This procedure seems to result in a higher microvoid content than does removal of monomer at $T > T_g$ (path ADC) or later heating above T_g (path CDC). Variations in the subsequent sorption of VCM at low activity reflect these history variations and seem to provide a measure of the microvoid content of PVC samples.

This earlier work clearly established the dual-mode and history-dependent nature of sorption in the VCM/PVC system. Other published studies of sorption in PVC seem limited to gaseous penetrants, as opposed to organic vapors. Tikhomirov, *et al.* (6) studied the transport of a number of permanent gases in PVC films, but did not specifically investigate history effects or isotherm curvature. Barrer, Mallinder, and Wong (7) found that the solubility of hydrogen and neon was affected by the thermal history of PVC films and suggested that pre-existing sorption sites, or "microgaps", play a role in sorption of these gases below T_g.

The present study was undertaken to determine whether the dual-mode, history-dependent behavior observed for VCM sorption in PVC might be generally characteristic of the sorption of other penetrants in glassy PVC. A gravimetric method and two novel volumetric techniques were employed to determine the amount of sorption and the form of sorption isotherms for several gases and organic vapors in PVC powders. Results obtained with polymer samples of varied history were analyzed through the dual-mode model (2) to ascertain whether history effects may be associated with a particular mode of sorption.

A complementary study of sorption in PVC powders using the technique of inverse gas chromatography will be reported separately (8).

EXPERIMENTAL

Materials

The PVC samples studied include commercial and experimental polymers polymerized by suspension and emulsion techniques. These were used in the powder form obtained directly from the polymerization. Samples designated as "never-heated" were recovered and dried at temperatures not exceeding the 50°C temperature of polymerization. "Heat-treated" samples, unless otherwise noted, were heated 1 h at 100°C and cooled slowly to room temperature. A sample of extruded, unplasticized PVC film, ~50 μm thick, was used in a few experiments. Gases and solvents were research grade, used without further purification.

Equipment and Procedures

Gravimetric sorption experiments were performed with the Cahn recording microbalance, vacuum system, and procedures described previously (1).

Volumetric gas sorption data were obtained with a Beckman Model 930 Air Comparison Pycnometer (Beckman Instrument Corp.). This instrument, shown schematically in *Fig. 4*, consists essentially of two matched cylinders with crank-driven pistons, connected through a differential pressure indicator; gas connections, valves, and a pressure gage permit evacuation, purging, and filling with a known pressure of selected gas. A weighed polymer sample is enclosed in the measuring cylinder, B, and cylinder A serves as a reference volume. The total enclosed volume of cylinder B

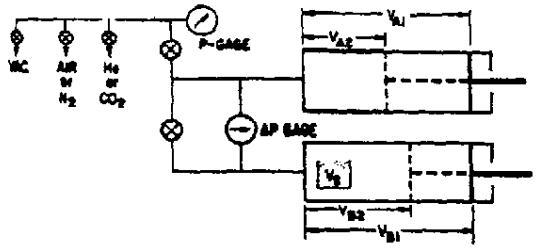

Fig. 4. Schematic diagram of Beckman gas pycnometer.

can be measured with a built-in counter, and a pointer and scale were added to cylinder A to permit reading of its enclosed volume. In operation, the enclosed volumes of the cylinders, V_{A_1} and V_{B_1}, are noted; the valves are then closed and the pistons advanced, while keeping the differential pressure at zero, increasing the pressure in both cylinders to $P_2 = -2\ P_1$, and decreasing the enclosed volumes to V_{A_2} and V_{B_2}. If the gas is not sorbed by the polymer sample, and ideal gas behavior is assumed, then in cylinder A,

$$P_1 V_{A_1} = P_2 V_{A_2} \tag{1}$$

and in cylinder B

$$P_1 (V_{B_1} - V_S) = P_2 (V_{B_2} - V_S) \tag{2}$$

where V_S is the volume of the polymer sample. Combining *Eqs 1* and *2* and solving for V_S gives

$$V_S = \frac{V_{A_2} V_{B_1} - V_{A_1} V_{B_2}}{V_{A_2} - V_{A_1}} \tag{3}$$

For a gas which is appreciably sorbed by the polymer, at P_1 the weight of free gas in cylinder B, w_1, is

$$w_1 = \frac{MP_1}{RT} (V_{B_1} - V_S) \tag{4}$$

and at P_2

$$w_2 = \frac{MP_2}{RT} (V_{B_2} - V_S) \tag{5}$$

where M is the gas molecular weight, R the gas constant, and T the temperature of measurement. The weight of gas sorbed by the polymer upon increasing pressure from P_1 to P_2, Δw, is therefore

$$\Delta w = w_1 - w_2$$

$$= \frac{M}{RT} [P_1 (V_{B_1} - V_S) - P_2 (V_{B_2} - V_S)] \tag{6}$$

A sorption coefficient, $\Delta w/g\Delta P$, may be defined as the weight of gas sorbed by a unit weight of polymer per unit increase in pressure, with g the sample weight and $\Delta P = P_1 - P_2$. By combining *Eqs 1* and *6*, it can be shown that

$$\Delta w/g\Delta P = \frac{M}{gRT} \left[\frac{V_{A_2}(V_{B_1} - V_S) - V_{A_1}(V_{B_2} - V_S)}{V_{A_2} - V_{A_1}} \right] \tag{7}$$

Pycnometer measurements with helium were used to obtain V_S, and *Eq 7* was applied to pycnometer data for N_2 and CO_2 to yield sorption coefficients, $\Delta w/g\Delta P$, for these gases in PVC powders. The assumption of ideal gas behavior in these calculations introduces an error of <2 percent in the worst case (CO_2 at 4 atm pressure).

Additional volumetric gas sorption data were obtained with a Digisorb 2500 automatic surface area analyzer (Micromeritics Instrument Corp.). This computer-controlled instrument is designed for automatic determination of sorption isotherms and ordinarily is used to determine B.E.T. surface areas of solid samples by adsorption of gases at liquid nitrogen temperature. By a simple modification of the computer program, solubility isotherms were obtained for N_2 and CO_2 up to atmospheric pressure in PVC samples at room temperature.

RESULTS AND DISCUSSION

Gaseous penetrants

Helium. The solubility coefficient for helium in PVC at 25°C reported by Tikhomirov, *et al.* (6) is 7.3×10^{-3} cc STP/cc PVC cm Hg, or 7×10^{-4} mg/g PVC-atm. Since the useful sensitivity of the Cahn balance is about 10^{-2} mg/g, gravimetric sorption measurements with helium were not attempted. Helium sorption experiments with the Digisorb 2500 were precluded by the requirement for calibration of the instrument "dead volume" with helium.

Because the solubility of helium in PVC is below the sensitivity of the Beckman pycnometer, gas pycnometry with helium may be employed to measure displacement volumes and densities within the instrument accuracy of about ±1 percent. In the course of this work, measurement of helium displacement volumes indicated a density of 1.404 ± 0.014 g/cm³ for nearly 80 PVC powder samples of widely varied history and particle structure. This value agrees well with the density of molded PVC specimens. Within the accuracy limits of the helium pycnometric method, no effect of thermal history upon the density of PVC could be detected.

Nitrogen. The solubility coefficient for N_2 in PVC at 25°C (3.1×10^{-4} cc STP/cc PVC cm Hg or 0.021 mg/g-atm (6)) is too low for precise gravimetric sorption experiments. Although the precision of the pycnometric method is insufficient for quantitative measurements of N_2 solubility, displacement volumes of PVC powders obtained through *Eq 1* from pycnometry with N_2 were invariably lower than those with helium, indicating a significant sorption of N_2. These data indicate a generally higher N_2 solubility in "never-heated" than in heat-treated PVC samples.

Use of the Digisorb 2500 instrument for N_2/PVC sorption measurements provides a substantial improvement in precision over gas pycnometry. Isotherms obtained at 29°C for N_2 in "never-heated" and heat-treated samples of a suspension-polymerized PVC powder are presented in *Fig. 5*. These results confirm the magnitude and history-dependence of the pycnometric sorption coefficients. The total sorption at atmospheric pressure for the heat-treated sample, 0.035 mg N_2/g PVC, agrees fairly well with the sorption coefficient given by Tikhomirov, *et al.* (6), but the "never-heated" sample sorbed about twice this amount of N_2 under the same

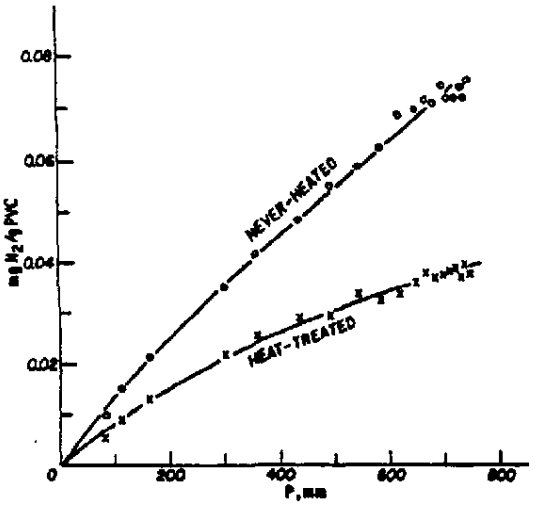

Fig. 5. Sorption isotherms for N_2 in suspension PVC at 29°C; Digisorb 2500 data.

conditions. Significantly, isotherms showing the downward curvature characteristic of dual-mode sorption are clearly defined by the Digisorb 2500 data despite the low total sorption in these experiments.

Carbon Dioxide. The relatively high solubility of CO_2 in PVC allows precise sorption experiments on this system with both volumetric and gravimetric techniques. Sorption isotherms determined gravimetrically at 25°C on "never-heated" and heat-treated samples of an emulsion-polymerized PVC powder are shown in *Fig. 6*, and 25°C isotherms obtained with the Digisorb 2500 for a similarly treated pair of suspension-type PVC's are shown in *Fig. 7*. The two techniques for measuring sorption are in excellent agreement, both clearly showing isotherm curvature of dual-mode form and a reduction in CO_2 solubility following heat treatment.

The apparent solubility coefficients corresponding to the total CO_2 sorption at atmospheric pressure in these experiments are appreciably larger than the coefficients obtained by Tikhomirov, *et al.* (6) from time-lag/permeation experiments. It seems likely that the coefficients of Tikhomirov, *et al.* are in error, since apparent, rather than true, diffusivities were presumably obtained from their measured time lags, and the solubility calculated from permeability and apparent diffusivity ignores the contribution of immobilized penetrant (Langmuirian sorption) to the total concentration of sorbed CO_2.

The equilibrium uptake of CO_2 by a rigid PVC film was very similar to that of the heat-treated powder (see *Fig. 6*); it therefore seems unlikely that surface adsorption plays a significant role in CO_2 sorption by these PVC powders.

Measurements with CO_2 in the Beckman pycnometer have been performed using a range of initial pressures, P_1, from 25 to 200 kPa (0.25 to 2 atm). Values of $\Delta w/g\Delta P$ obtained for "never-heated" and heat-treated portions of a suspension-type PVC powder are plotted as a function of P_1 in *Fig. 8*. Since $\Delta w/g\Delta P$ corresponds to the secant slope of the sorption isotherm between P_1 and $P_2 \cong 2P_1$, the pycnometer data can be compared with the gravimetric and Digisorb isotherms (*Figs. 6* and *7*). Excellent agreement is found among these three sets of data. All show the marked reduction of CO_2 sorption following heat treatment; the decrease of $\Delta w/g\Delta P$ with

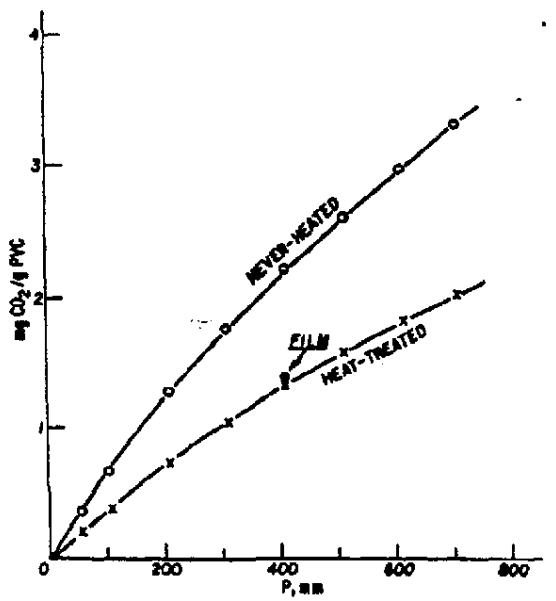

Fig. 6. Sorption isotherms for CO_2 in emulsion PVC at 25°C, gravimetric data.

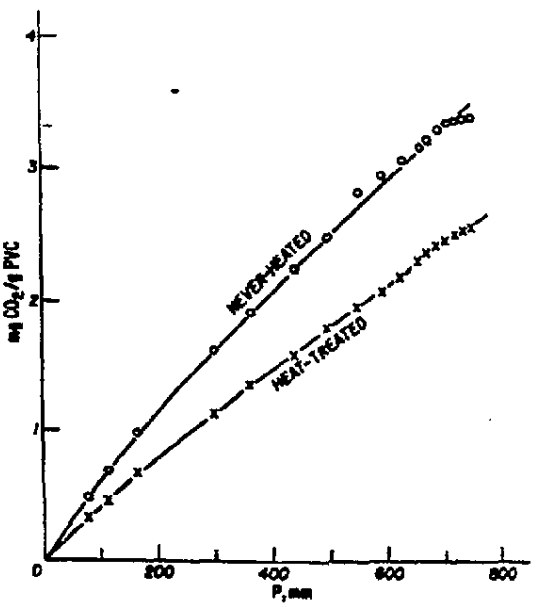

Fig. 7. Sorption isotherms for CO_2 in suspension PVC at 25°C, Digisorb 2500 data.

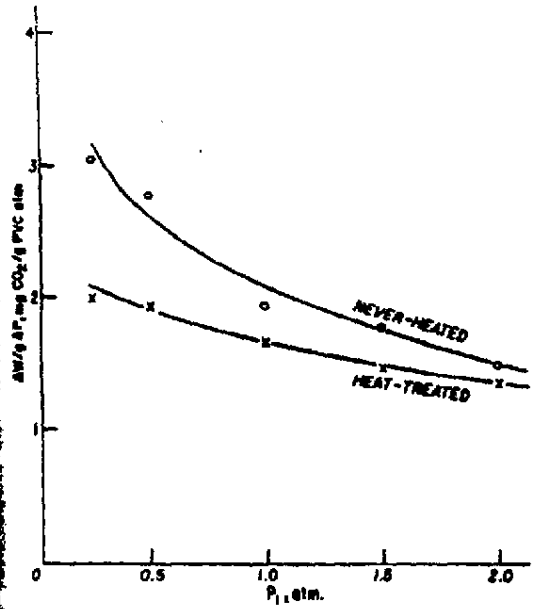

Fig. 8. Secant sorption coefficients, $\Delta w/g\Delta P$, for CO_2 in suspension PVC at 25°C, gas pycnometer data at varied P_1.

increasing P is consistent with the isotherm curvature; and the values of $\Delta w/g\Delta P$ agree well with the slopes of the isotherms at corresponding pressures.

The composite CO_2 sorption data provide a means of estimating the parameters of the dual-mode model, which is generally expressed (2) in the form

$$C = C_D + C_H = k_D P + \frac{C'_H bP}{1 + bP} \qquad (8)$$

Here C is the total sorption, C_D the contribution of normal dissolution, C_H the hole-filling or Langmuirian contribution, k_D the Henry's Law constant, C'_H the sorption capacity of the "holes" at saturation, and b the hole affinity constant. The usual procedure for evaluating the model parameters is to obtain k_D from the asymptotic slope of C vs P at high P, subtract $k_D P$ from C to obtain C_H, then determine C'_H and b from the slope and intercept of "Langmuir plots" (either $1/C_H$ vs $1/P$ or P/C_H vs P). The pycnometric daata shown in *Fig. 8* suggest that the sorption coefficients for both samples approach a common asymptotic value of approximately 1 mg/g-atm (0.7 cc STP/cc-atm). Using this figure as an estimated k_D, Langmuir plots were constructed from the gravimetric and Digisorb data of *Figs. 6* and *7*. Linear plots were obtained in all cases, supporting the applicability of the dual-mode model. The slopes and intercepts of these plots yielded values of C'_H from 2.5 to 7.1 mg/g-atm (1.8 to 5.1 cc/cc-atm), and of b from 0.4 to 0.8 atm^{-1}. The magnitude of these parameters is consistent with those reported for CO_2 in other glassy polymers, e.g., polyethylene terephthalate (2), polystyrene (9), and ethyl cellulose (10).

Comparison of the CO_2 sorption results for "never-heated" and heat-treated PVC samples suggests an interesting relation between thermal history and sorption parameters. The apparent common asymptote of the $\Delta w/g\Delta P$ vs P curves (*Fig. 8*) indicates that k_D, which reflects the contribution of normal dissolution, is independent of thermal history. A measure of the contribution nf Langmuirian sorption relative to normal dissolution, at very low CO_2 pressure, is given by the ratio $C'_H b/k_D$. For "never-heated" samples, the gravimetric data on emulsion PVC give $C'_H b/k_D = 4.3$, and the Digisorb data on suspension PVC give $C'_H b/k_D = 3.8$; the corresponding figures for the heat-treated samples are 2.0 and 2.2. Thus the history-dependence of CO_2 sorption appears related predominantly to the Langmuirian or hole-filling term in the dual-mode model. This relation, in turn, seems to support the inference drawn from VCM sorption studies (5) that post-polymerization thermal history controls the hole or microvoid content of PVC samples.

Further data on the relation between sample history and inferred microvoid content have been obtained from gas pycnometer solubility measurements with CO_2 on PVC powders heat-treated at varied temperatures. Data were taken at low P_1 (0.25 atm) where history effects are most pronounced. *Figure 9* shows $\Delta w/g\Delta P$ as a function of annealing temperature for portions of a PVC previously not heated above 50°C. Annealing at temperatures up to T_g produced a significant reduction in microvoid content measured by CO_2 sorption.

Organic Vapors

The study of organic vapor sorption in glassy polymers, as compared to that of gases, is complicated by two significant factors: the much lower diffusivity of the larger vapor molecules greatly retards the attainment of diffusion equilibrium, and sorption experiments can be performed on a convenient time scale only with fine

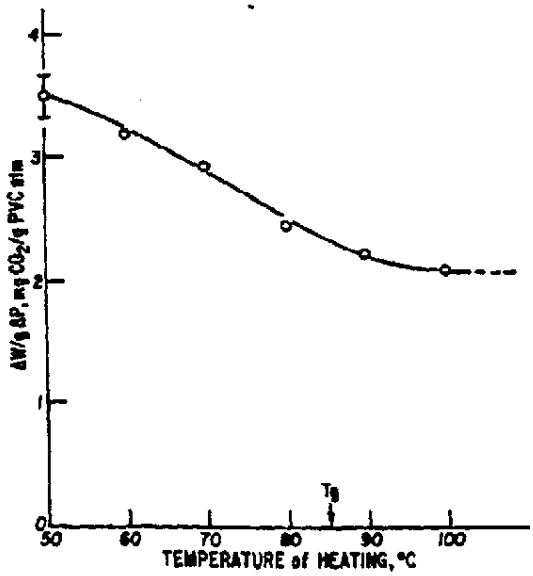

Fig. 9. Sorption coefficients, $\Delta w/g\Delta P$, for CO_2 in PVC samples heat-treated 3 h at varied temperature, gas pycnometer data.

powder samples (11). The occurrence of relaxation-controlled swelling, which may be responsible for a significant portion of the total sorption when a glassy polymer is exposed to an organic vapor, also complicates the analysis (11, 12). Previous study of the effects of time and sample history on vapor sorption isotherms suggest that different levels of "equilibrium" should be considered in glassy polymer/organic vapor systems (13). The attainment of a uniform penetrant concentration in the polymer represents "diffusion equilibrium", which can be approached in a few minutes, or less, in fine powders. "Relaxation equilibrium" may be said to occur when the second-stage, relaxation sorption has ceased or slowed to an immeasurable rate; days or weeks may be required to reach this point. Separation of the contributions of relaxation and diffusion controlled sorption appears possible in experiments with fine powders, as diffusion equilibration may be approached before significant relaxation occurs (12). Short-time sorption experiments have been used here to estimate the "quasi-equilibrium" solubility of organic vapors in glassy PVC before the occurrence of a significant relaxation-controlled swelling.

Vinyl Chloride. The previously published sorption "isotherms" for the VCM/PVC system (1) were obtained from experiments in which the VCM pressure was increased incrementally over periods of many hours; the sorption therefore included a substantial contribution from relaxation/controlled swelling. To minimize this effect, gravimetric sorption data have been obtained for brief (≤ 1 min) exposures of PVC samples to VCM vapor at a succession of pressures; between exposures, samples were held under vacuum for at least 30 min. The PVC used in these experiments was a monodisperse emulsion polymer of 0.11 μm particle diameter; its calculated half-sorption time for Fickian diffusion of VCM at 30°C ($D \cong 2 \times 10^{-12}$ cm²/s) (10) was less than one second. The amounts of VCM sorbed in 30 s could thus be taken to represent "diffusion equilibrium" with a negligible contribution of relaxation. The 30 s VCM sorption data obtained at 30°C for "never-heated" and heat-treated portions of this PVC are plotted against the relative pressure of VCM ($P_{rel} = P/P_s$, $P_s = 4.55$ atm) in *Fig. 10*.

The isotherms defined by these short-time VCM sorption data again show "dual-mode" curvature and a marked dependence on sample history. Moreover, the data for both samples appear to approach an asymptotic slope equal to the low-activity limiting slope (88 mg/g P_{rel} or 19.3 mg/g-atm) of the Flory-Huggins curve determined from earlier work at higher VCM pressures (1). This value was taken as k_D in order to estimate the parameters of the dual-mode model from the linear Langmuir plots. For the "never-heated" sample, the values found were $C'_H = 3.6$ mg/g, $b = 29$ atm^{-1}, and for the heat-treated sample, $C'_H = 1.8$ mg/g, $b = 43$ atm^{-1}. These results yield values of 5.3 and 3.9, respectively, for the ratio C'_Hb/k_D in never-heated and heat-treated samples, significantly higher than the corresponding values in CO_2 sorption. From the VCM results, as with CO_2, it appears that the effect of thermal history is associated with the hole-filling term, rather than the Henry's Law term, of the dual-mode model.

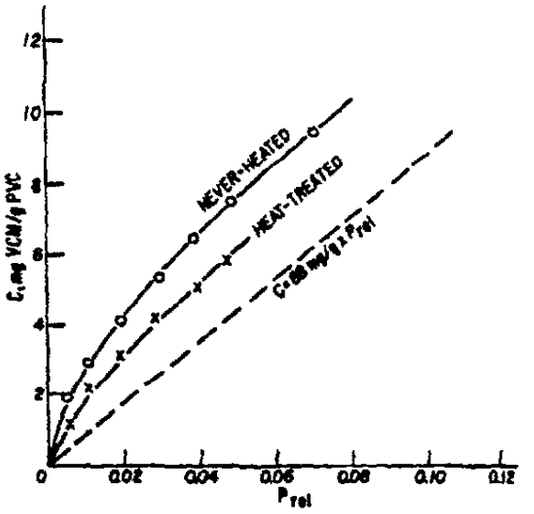

Fig. 10. Sorption isotherms for VCM in 0.11 μm emulsion PVC at 30°C, gravimetric data, 30 s sorption time.

Methanol. Short-time gravimetric sorption data for methanol vapor with never-heated and heat-treated samples of a suspension-type PVC powder at 40°C are shown in *Fig. 11*, plotted against the relative pressure of methanol ($P_o = 260$ mm Hg). For these PVC samples, the estimated half-sorption time for Fickian diffusion of methanol is approximately 5 s; the plotted 1 min sorption values, therefore, represent estimates of the "equilibrium" uptake before appreciable relaxation occurs. The data define isotherms of dual-mode form which approach a similar asymptotic slope for both samples. The dual-mode parameters obtained from these data for the never-heated sample are $k_D = 31.9$ mg/g-atm, $C'_H = 1.89$ mg/g, $b = 22$ atm^{-1}, and for the heat-treated sample, $k_D = 27.2$ mg/g-atm, $C'_H = 0.50$ mg/g, $b = 54$ atm^{-1}. Once again, the effect of sample history appears principally associated with the hole-filling term of the dual-mode model.

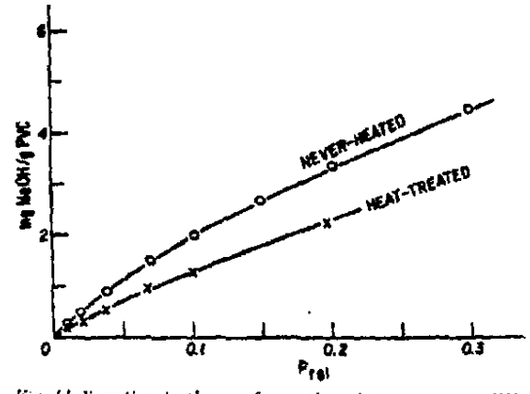

Fig. 11. Sorption isotherms for methanol in suspension PVC at 40°C; gravimetric data, 1 min sorption time.

Fig. 12.
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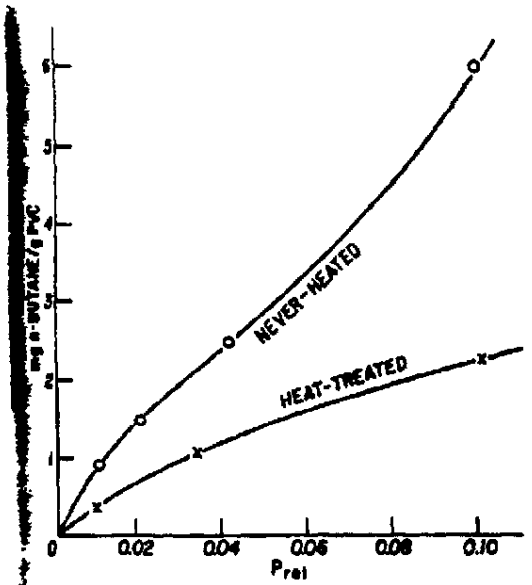

Fig. 12. Sorption isotherms for n-butane in emulsion PVC at 30°C, gravimetric data, sorption times ~18 h.

Other Organic Vapors. Gravimetric sorption measurements have also been carried out on PVC samples of differing history with acetone, butane, and benzene vapors at low activities. The data are not sufficiently extensive, however, to allow quantitative estimation of the dual-mode parameters. Moreover, the diffusivities of these larger molecules are too low for unambiguous determination of sorption unconfounded by relaxation effects. The data shown in *Fig. 12* were obtained for the n-butane/PVC system at 30°C in experiments involving 18 h of contact at each pressure. Similar results have also been obtained for acetone and benzene. Despite the substantial contribution of relaxation to the overall sorption, the general dual-mode character and pronounced history-dependence of the data are clear for all penetrants studied.

CONCLUSIONS

The consistent evidence from three independent experimental techniques presented here shows that the sorption of a wide variety of gases and organic vapors in glassy PVC follows the dual-mode sorption theory and also depends upon the post-polymerization thermal history of the polymer sample. Generally similar behavior is observed for penetrant molecules differing widely in size, polarity, and affinity for PVC. In the cases where the data permit estimation of the individual parameters of the dual-mode model, i.e., carbon dioxide, vinyl chloride, and methanol, the history-dependence of sorption appears to be related to the hole-filling term, rather than the normal dissolution term, of the model. This result lends support to earlier inferences (5) that the major effect of post-polymerization history variations on PVC is to alter the polymer's content of frozen-in holes or microvoids.

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REFERENCES

1. A. R. Berens, *Angew. Makromol. Chem.*, **47**, 97 (1975).
2. A. S. Michaels, W. R. Vieth, and J. A. Barrie, *J. Appl. Phys.*, **34**, 1 (1963).
3. I. Yu. Ibragimov, D. N. Bort, and V. N. Efremova, *Vysokomol. Soedin. Ser. B.*, **16**, 376 (1974).
4. N. Friis and A. E. Hamielec, *ACS Symposium Series No. 24*, 82 (1976).
5. A. R. Berens, *J. Macromol. Sci.-Phys.*, **B14**, 483 (1977).
6. B. P. Tikhomirov, H. B. Hopfenberg, V.T. Stannett, and J. L. Williams, *Makromol. Chem.*, **118**, 177 (1968).
7. R. M. Barrer, R. Mallinder, and P. S.-L. Wong, *Polymer*, **8**, 321 (1967).
8. A. R. Berens, to be published.
9. W. R. Vieth, P. M. Tam, and A. S. Michaels, *J. Colloid Interface Sci.*, **22**, 360 (1966).
10. A. H. Chan, W. J. Koros, and D. R. Paul, *J. Membrane Sci.*, **3**, 117 (1978).
11. A. R. Berens, *Polymer*, **18**, 697 (1977).
12. A. R. Berens and H. B. Hopfenberg, *Polymer*, **19**, 489 (1978).
13. A. R. Berens, *J. Membrane Sci.*, **3**, 247 (1978).