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Diffusion in Glassy Polymers. III. Temperature Dependence and Solvent Effects

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Absorption and desorption of benzene and ethyl acetate by atactic polystyrene (A-PS) were studied at various temperatures below the glass transition point of the polymer. In the A-PS+benzene system raising temperature did not alter the general feature of the family of successive differential absorption curves, but merely compressed the whole family of curves towards a low concentration region. The critical concentration of penetrant at which the transition from non-Fickian to Fickian behavior occurred became lower in the order benzene, ethyl methyl ketone, and ethyl acetate. The logarithm of the time, t_*, which specifies the inflection point of the second stage on the two-stage absorption curve, were linearly dependent on the initial concentration of penetrant, C_i, and the correlation lines between log t_* and C_i obtained for various combinations of temperature and solvent were nearly parallel with one another. The features of integral absorptions were essentially the same in all cases, and the absorption curves showed a pronounced dependence on concentration.

Recent studies of absorption and desorption of organic vapors by amorphous polymers have shown that when the polymer is in the glassy state these processes do not conform to the Fickian type; that is, the Fick diffusion equation with a concentration dependent diffusion coefficient and with the usual boundary conditions is not obeyed.¹⁾ It is generally accepted that these non-Fickian processes are controlled not only by the ordinary diffusion mechanism but also by the relaxation mechanism of polymer network chains. When the polymer is in the glassy state the rate at which the network of polymer chains responds to the osmotic swelling pressure is so slow that the rate of absorption or desorption of organic vapors by the polymer may depend markedly upon both temperature and penetrant concentration. However, our present knowledge²⁻⁶⁾ about this problem is insufficient or otherwise incomplete. For example, data on the temperature dependence of the successive differential absorption are as yet not available. The first purpose of the present work is to find out how the behavior of successive absorption processes in systems of amorphous polymer and organic vapor is affected by temperature. To this end we have studied the system atactic polystyrene (A–PS) and benzene.

In a recent publication,⁷⁾ we showed that the general features of the family of successive

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1) For a review of recent studies in the field, see H. Fujita, *Fortschr. Hochpolymer.-Forsch.*, **3**, 1 (1961).

2) G. S. Park, *Trans. Faraday Soc.*, **46**, 684 (1950).

3) A. T. Hutcheon, R. J. Kokes, J. L. Hoard and F. A. Long, *J. Chem. Phys.*, **20**, 1232 (1952).

4) R. J. Kokes, F. A. Long and J. L. Hoard, ibid., **20**, 1711 (1952).

5) F. A. Long and R. J. Kokes, *J. Am. Chem. Soc.*, **75**, 2232 (1953).

6) R. J. Kokes and F. A. Long, ibid., **75**, 6142 (1953).

7) H. Odani, J. Hayashi and M. Tamura, This Bulletin, **34**, 817 (1961).

differential absorption curves for the A-PS+ethyl methyl ketone system was similar to those obtained for the A-PS+benzene system. However, for the ethyl methyl ketone system, the critical concentration at which the polymer-penetrant mixture underwent glass transition at the temperature of the experiment was lower than that for the benzene system, and the characteristic variation of the types of successive differential absorption curves occurred in a relatively lower concentration region. In either of these systems, the second stage portion of the two-stage process shifted rapidly to the short time region as the initial concentration of each step was increased. To express this rate of shift the time t_* for the inflection point of each differential absorption curve was taken as the measure of the location of the second stage portion on the time axis. The plots of the logarithm of t_* against the initial concentration C_i was linear. The slopes of the lines were nearly the same. Ethyl methyl ketone and benzene have nearly the same molar valumes, but the former is less soluble in A-PS than is the latter. To confirm these features and other effects of polymer-penetrant interaction upon absorption and desorption kinetics, we have made similar measurements with the system A-PS and ethyl acetate and have compared the results with our previous results with the benzene system and the ethyl methyl ketone system. These three penetrants have about the same molar volumes, but have different solvent powers for A-PS. The values of the interaction parameter χ_1 of A-PS at 25°C are 0.55, 0.53, and 0.45 for ethyl acetate, ethyl methyl ketone, and benzene, respectively.⁸⁾ Thus the solvent power for A-PS becomes larger in the order ethyl acetate, ethyl methyl ketone, and benzene.

Experimental

The atactic polystyrene (A-PS) used was the same as that described previously.⁹⁾ Its viscosity-average molecular weight was 2.2×10^5. The films used for sorption measurements were approximately 2.4×10^{-3} cm. thick. Benzene and ethyl acetate used as organic penetrants were of G. R. grade, and no attempt was made to effect further purification. The temperatures at which the sorption measurements were performed were 25, 35, and 50°C for A-PS+benzene and 25°C for A-PS + ethyl acetate. These temperatures are well below the glass transition temperature of the dry polymer.¹⁰⁾

Results and Discussion

Absorption Isotherms.—Absorption isotherm data for the system A-PS+benzene at 25, 35, and 50°C are given in Fig. 1. Here the ordinate represents the mass of absorbed vapor in grams per unit gram of dry polymer and the abscissa the relative pressure of the vapor in the external phase. Although the individual points are not given in the figure, at a given relative pressure the differences in equilibrium gain between integral and differential absorption experiments were negligible at the three temperatures examined (Data at 25°C are shown later in Fig. 2.). It is seen that the data for 25 and 35°C are nearly represented by a single curve, indicating that the isotherms are practically independent of temperature within this narrow range of temperature. The data of Long and Kokes at 40°C⁵⁾ are also included in the figure for comparison. Formal application of the Flory-Huggins thermodynamic equation of polymer solutions, with the assumption that no volume change occurs on mixing, shows that at each temperature the interaction parameter χ_1 increases slightly with increase of equilibrium vapor concentration. The average values of χ_1 over the concentration range studied, except at very low penetrant concentrations, were 0.14, 0.14, and 0.32 at 25, 35, and 50°C, respectively. The average value of χ_1 evaluated from the data of Long and Kokes⁵⁾ was 0.27 at 40°C.

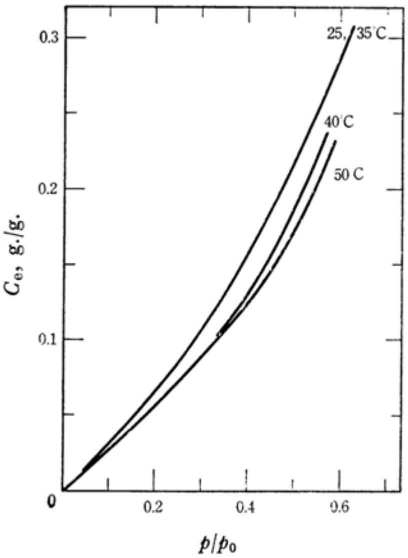

Fig. 1. Absorption isotherms of A-PS+benzene at 25, 35, and 50°C.

Figure 2 compares absorption isotherm data for the system A-PS+ethyl acetate, the system A-PS+benzene, and the system A-PS + ethyl methyl ketone,⁷⁾ all at 25°C. As expected, it can be seen that the equilibrium mass of absorbed penetrant

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8) R. F. Boyer and R. S. Spencer, *J. Polymer Sci.*, **3**, 97 (1948).

9) A. Kishimoto, H. Fujita, H. Odani, M. Kurata and M. Tamura, *J. Phys. Chem.*, **64**, 594 (1960).

10) H. Mark and A. V. Tobolsky, "Physical Chemistry of High Polymeric Systems," Interscience Pub. Inc., New York (1950), p. 347.

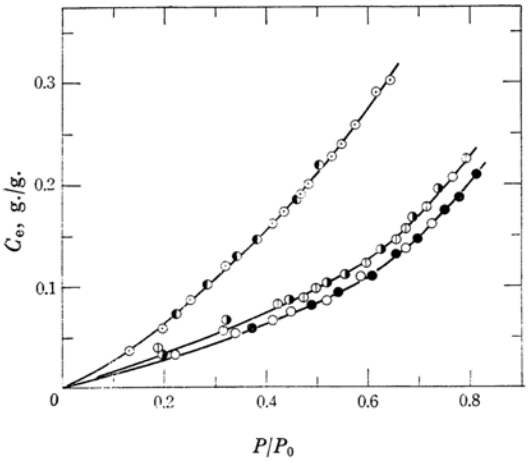


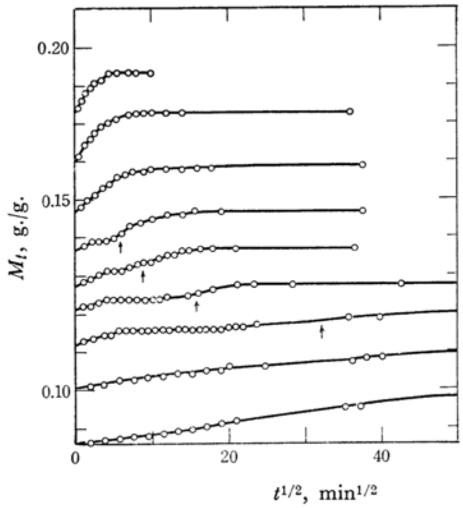
Fig. 2. Absorption isotherms of A-PS+ethyl acetate, A-PS+benzene, and A-PS+ethyl methyl ketone at 25°C.

	Integral absorption	Differential absorption
A-PS+ethyl acetate	○	●
A-PS+benzene	⊙	◐
A-PS+ethyl methyl ketone	⦶	◑

becomes less in the order benzene, ethyl methyl ketone, and ethyl acetate when compared at the same relative vapor pressure of penetrant. That is, at a given relative vapor pressure, the poorer the solvent power to a given polymer the lower is the equilibrium vapor absorption. The values of the interaction parameter χ_1 calculated from these isotherm data at 25°C were 0.97 and 0.78 for A-PS+ethyl acetate and A-PS+ethyl methyl ketone, respectively.

Successive Differential Absorptions.— Figure 3 gives the data of successive differential absorptions for the system A-PS+benzene at 35°C in the medium and high concentration regions. The increments of benzene concentration in successive steps were kept about 0.01 g. penetrant per gram of dry polymer, which was almost the same as those used in our previous experiments.[7,9] Although the results in the low penetrant concentration region are not given in the figure, the general character of the absorption steps in this region was quite similar to that for the system polymethyl methacrylate+methyl acetate at 30°C.[9] That is, the absorption behavior was of the sigmoid type. The inflection point characteristic of the sigmoid curve shifted toward the short time region and the initial rate of each absorption increased as the initial concentration was increased. The first step in Fig. 3 exhibits a sigmoid character, and the subsequent absorption curves change their type according to the following scheme: pseudo-Fickian→two-stage→Fickian. As noted in the previous paper,[9] the data for the A-PS+benzene system did not show a pseudo-Fickian process in the transition from the two-stage to the normal Fickian process.

With increasing temperature the concentration at which the absorption curve change their type from sigmoid to pseudo-Fickian behavior shifted toward low concentration values, and this was also the case with the initial concentration at which the transition from the pseudo-Fickian to the two-stage and from the two-stage to the Fickian occurred. In other words, raising temperature did not alter the general features of the family of successive differential absorption curves but merely compressed the whole family of curves to a lower concentration region. It has been demonstrated



Pressure p_i mmHg		Interval p_f mmHg
63	→	66
59	→	63
56	→	59
53	→	56
50	→	53
47	→	50
45	→	47
42	→	45
37	→	42

Fig. 3. Successive differential absorptions of A-PS+benzene at 35°C. Initial and final pressures, p_i and p_f, of each step are given in the right columns.

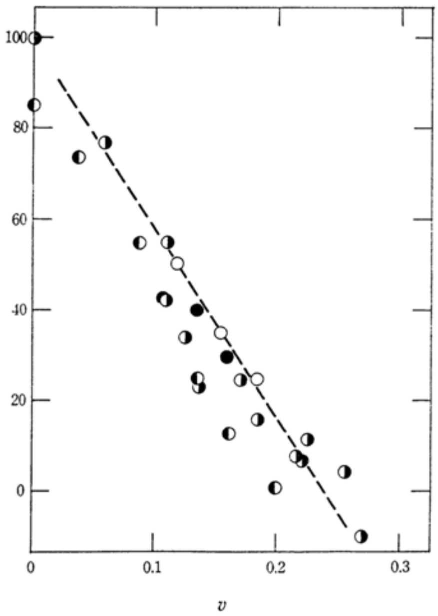


Fig. 4. Comparison of volume fraction for glass transition with critical volume fraction for diffusion.

○, Differential absorption experiments;
●, Sorption experiments by Long and Kokes⁵⁾;
◑, Dilatometric studies by Fox¹¹⁾;
◐, Refractive index studies by Jenckel and Heusch.¹²⁾

in the previous papers⁷⁾,⁹⁾ that successive differential absorption curves change their type from non-Fickian to Fickian when the penetrant concentration reaches a value at which the polymer-penetrant mixture undergoes glass transition at the temperature of the experiment. From differential absorption data obtained with concentration intervals of nearly the same magnitude as those shown in Fig. 3, we estimated such a critical concentration for the A-PS+benzene system to be 0.150 at 35°C and 0.113 at 50°C in grams of benzene per gram of dry polymer. At 25°C the critical concentration of benzene was 0.191 g./g.⁹⁾ In Fig. 4 the values for the critical volume fraction calculated from these data are compared with the results obtained from dilatometric studies by Fox,¹¹⁾ from refractive index studies by Jenckel and Heusch,¹²⁾ and from sorption experiments by Long and Kokes.⁵⁾ It can be seen that the points from different experimental techniques fall satisfactorily on a single line, indicating that the glass transition is closely related to the molecular mechanism which distinguishes Fickian absorption behavior of an amorphous polymer-penetrant system from non-Fickian.

The successive differential absorption data for A-PS+ethyl acetate at 25°C showed features which were quite similar to those of A-PS+ethyl methyl ketone at 25°C investigated previously.⁷⁾ That is, the successive curves change their type with increasing penetrant concentration according to the scheme: sigmoid→pseudo-Fickian→two-stage→pseudo-Fickian→Fickian. However, for A-PS+ethyl acetate the critical concentration was 0.112 in grams of ethyl acetate per gram of dry A-PS. This value is well consistent with the data interpolated from refractive index measurements of Jenckel and Heusch,¹²⁾ but lower than 0.139 g./g. obtained previously for ethyl methyl ketone at the same temperature. In the previous paper,⁷⁾ from comparison of the critical concentrations of ethyl methyl ketone and of benzene, we suggested that for an amorphous polymer at a given temperature a penetrant of poorer solubility gives a lower critical concentration if comparison is made for penetrants of about the same molar volumes. As described in the foregoing lines, the molar volumes of ethyl acetate, ethyl methyl ketone, and benzene are nearly the same. Thus we find that the present result with the system A-PS+ethyl acetate is in line with the deduction from our previous results.⁷⁾,⁹⁾

Concentration Dependence of the Second Stage Mechanism.—It is generally accepted⁷⁾,⁹⁾ that the rate-determining factor for the second stage portion of the two-stage absorption is the rate at which polymer chains rearragne themselves in the presence of penetrant molecules, while the first stage involves the purely Fickian process. In accordance with the treatment presented in previous studies,⁷⁾,⁹⁾ we here use the time t_* to characterize the position of the second stage portion on the time axis, where t_* is the time corresponding to the inflection point of a differential absorption curve of the two-stage type. The previous study¹³⁾ demonstrated for the system A-PS+benzene at 25°C that the value of t_* for a given initial concentration, C_i, increased with decreasing concentration increment and converged to a limiting value taken as characteristic of the given C_i. This was also the case with the A-PS+benzene at 35 and 50°C. The values of t^* characteristic of a given C_i for the system A-PS+benzene at 25, 35, and 50°C are plotted semilogarithmically against C_i in Fig. 5. We see that the plots for different temperatures are linear and nearly parallel with one another, indicating that for a given amorphous polymer the slope of $\log_{10} t_*$ vs. C_i plot is approximately independent of temperature. Thus the plots for $\log_{10} t_*$ vs. C_i at different temperatures may be superimposed with one another by shifting each plot along the

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11) T. G. Fox. *Phys. Rev.*, **86**, 652 (1952).
12) E. Jenckel and R. Heusch, *Kolloid Z.*, **130**, 89 (1953).
13) H. Odani, S. Kida, M. Kurata and M. Tamura, This Bulletin, **34**, 571 (1961).

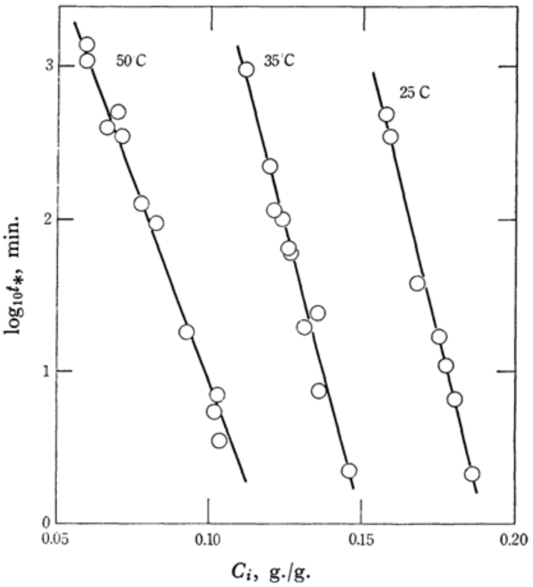

Fig. 5. Logarithmic correlation plots of t_* and initial concentration C_i for A-PS+benzene at 25, 35, and 50°C. t_* is the time corresponding to the inflection point of the second stage of the two-stage process.

ordinate to a particular temperature chosen as reference. This behavior bears resemblance to the time-concentration reduction scheme which was shown to be obeyed by stress-relaxation behavior of polymer-diluent systems in nearly the same concentration regions.14) In this connection, it is worth-while to note the correlation between t_* and the mean relaxation time or, more properly, retardation time. We have shown for the system A-PS+benzene that the values of the mean retardation time, evaluated from the tensile creep measurements, and their dependence upon C_i are closely correlated with the values of t_* and their dependence upon C_i*. These results lend support to the argument that the second stage of a two-stage absorption process is primarily caused by the slow rearrangements of polymer network chains. Plots for $\log_{10} t_*$ vs. C_i at higher temperatures appear in the region of lower values of C_i. This is the reflection of the fact that the value of C_i at which the transition from pseudo-Fickian to two-stage type absorption occurred shifts toward the lower concentration region with increasing temperature. The values of the apparent activation energy were estimated at $C_i=0.115$ and 0.110 g./g. based on the assumption that the temperature dependence of t_* follows the Arrhenius type equation. They were 64 and 46 kcal./mol., respectively. These values compare favorably with those obtained from the time-temperature shift factor for linear visco-elastic behavior of amorphous polymers in the temperature region near glass transition.

Plots of $\log_{10} t_*$ vs. C_i for the system A-PS+ethyl acetate at 25°C are illustrated in Fig. 6. For the sake of comparison, the corresponding data for A-PS+benzene, A-PS+ethyl methyl ketone, and cellulose nitrate+acetone are included in the figure. The slope of the line for A-PS+ethyl acetate is nearly the same as those for A-PS+benzene and A-PS+ethyl methyl ketone. These slopes for A-PS systems are greater than that for cellulose nitrate. In the previous paper,7) it was argued that the slopes of $\log_{10} t_*$ vs. C_i plot for a given polymer must be independent of penetrant species, because the second stage absorption primarily reflects the characteristic relaxation-motion of the network chains. Data for A-PS+ethyl acetate establish firmly this view. This, together with the results for the temperature dependence of $\log_{10} t_*$ vs. C_i plots shown in Fig. 5, clearly indicates that the second stage of the two-stage process is governed by the rate at which the network of polymer chains change its conformation under the osmotic swelling pressure.

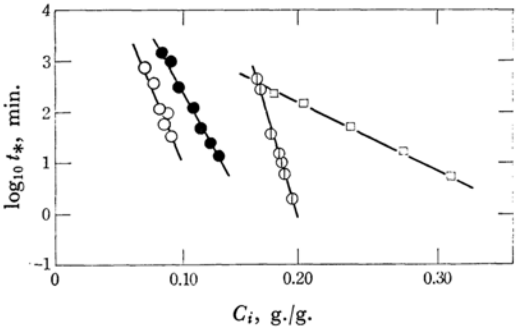

Fig. 6. Logarithmic correlation plots of t_* and initial concentration C_i for some polymer+vapor systems at 25°C.
○, A-PS+ethyl acetate;
⊖, A-PS+benzene;
●, A-PS+ethyl methyl ketone;
□, Cellulose nitrate+acetone.

Integral Absorptions and Desorptions.— The measurements of integral absorption and desorption with various pressure differences were carried out from and back to zero penetrant concentration. The general features of the integral absorption and desorption processes for A-PS+benzene at 35 and 50° were quite similar to those obtained previously at 25°C.13) That is, the integral absorption curves were sigmoid for all pressure intervals investigated. On the other hand, the integral absorption curves were concave to the $t^{1/2}$ axis, no linear portion was observed in

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14) H. Fujita and A. Kishimoto, *J. Polymer Sci.*, **28**, 547 (1958).

* Preliminary report of the tensile creep behavior of the system A-PS+benzene appeared in "*Rep. Progr. Polymer Phys. Japan*," **6**, 163 (1963). Detail will be reported in a forthcoming publication.

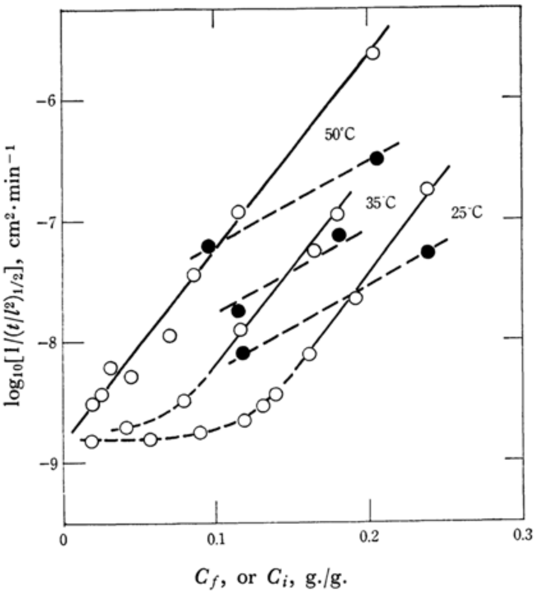

Fig. 7. Logarithmic correlation plots of $1/(t/l^2)_{1/2}$ and final equilibrium concentration, C_f, for absorption or initial concentration, C_i, for desorption for A-PS+benzene at 25, 35, and 50°C. $(t/l^2)_{1/2}$ is the value t/l^2 when the amount of vapor in polymer reaches one half of the final equilibrium value; l is the thickness of film and t is time. ○, absorption. ●, desorption.

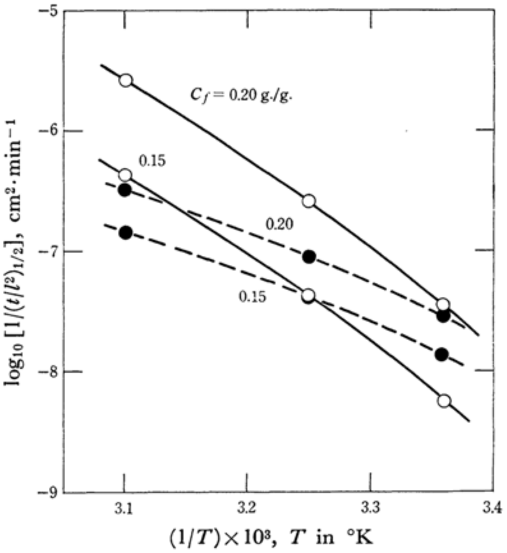

Fig. 8. Logarithmic correlation plots of $1/(t/l^2)_{1/2}$ and reciprocal absolute temperature for A-PS+benzene at C_f=0.15 and 0.20 g./g. ○, absorption. ●, desorption.

the initial stage, and the slope of the curve decreased continuously from the origin. The desorption curve had a much higher initial rate than that of the corresponding absorption and intersected with the latter in the later stage. At 35 and 50°C the absorption curves showed a pronounced dependence on the pressure difference and the general feature of this dependence was similar to that observed at 25°C. As noted in the previous report,[13] the absorption processes from zero to equilibrium concentrations above the critical concentration exhibited non-Fickian features contrary to the data of Long and Kokes,[5] who observed Fickian absorption curve in such cases. This was also the case at 35 and 50°C, and the non-Fickian behavior still persisted at the highest equilibrium concentration studied. At the highest concentration, which was far above the critical concentration, the polymer films hardly supported its own weight from the spring balance.

In the case when absorption and desorption curves do not conform to normal Fickian features, we are not able to evaluate the mutual diffusion coefficient of the system by using the methods which utilize data for the initial slope of the absorption curve. In such a case, as in the previous treatment,[7,13] we may be content with the reciprocal of $(t/l^2)_{1/2}$ being taken as a quantitative measure of the overall rate of an absorption or desorption curve, where l is the thickness of the film and $(t/l^2)_{1/2}$ is the value of t/l^2 for the time t at which the amount of penetrant in the film reaches one half the final equilibrium value. The values of $1/(t/l^2)_{1/2}$ for the system A-PS+benzene, determined from integral absorptions from and to zero penetrant concentration, are plotted semi-logarithmically against the equilibrium concentration, C_f, in Fig. 7. It is seen that at 25 and 35°C the plots from absorption data are convex to the concentration axis in the low concentration region and are linear at medium and high values of C_f. At 50°C. the plots increase linearly with increasing C_f over the entire range investigated. In the linear portion the plots for the three temperatures are nearly parallel and their slopes are larger than those for integral desorption. From this latter behavior it follows that the temperature dependence of sorption rate is greater for absorption than for desorption at fixed values of C_f, and it may be expected that for a glassy polymer the apparent activation energy for absorption is larger than that for desorption.

For a quantitative representation of the temperature dependence of the overall rate of absorption or desorption, we determined the apparent activation energy from the slope of a plot for the logarithm of $1/(t/l^2)_{1/2}$ against reciprocal absolute temperature. Figure 8, which illustrated such plots for A-PS+benzene at C_f=0.15 and 0.20 g./g., indicates that for both absorption and desorption the values of $\log_{10}[1/(t/l^2)_{1/2}]$ decrease nonlinearly with increasing $1/T$. This similar feature has been reported for diffusion coefficients of gases

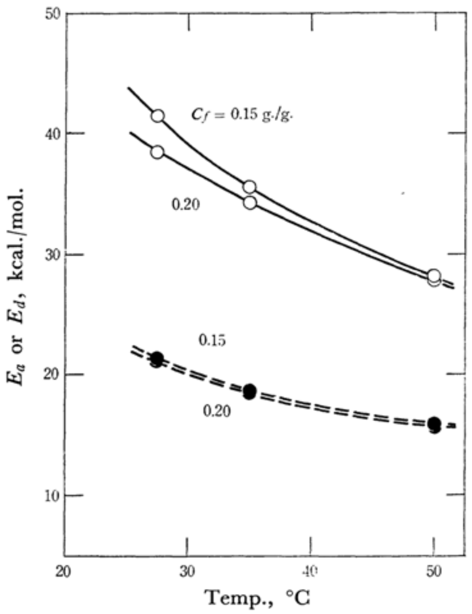

Fig. 9. Temperature dependence of the apparent activation energy for absorption, E_a, or for desorption, E_d, for A-PS+benzene at $C_f=0.15$ and 0.20 g./g. ○, absorption. ●, desorption.

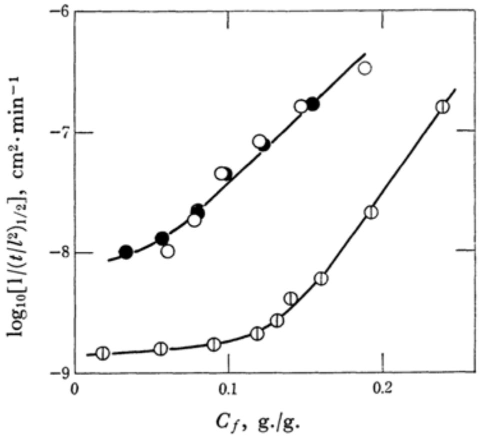

Fig. 10. Logarithmic correlation plots of $1/(t/l^2)_{1/2}$ and final equilibrium concentration C_f for A-PS +ethyl acetate, A-PS+benzene, and A-PS+ethyl methyl ketone at 25°C.
○, A-PS+ethyl acetate;
⦶, A-PS+benzene;
●, A-PS+ethyl methyl ketone.

or vapors in elastomers.[15-18]

An apparent activation energy for absorption, E_a, may be defined by the equation:

$$E_a = -Rd\{\ln[1/(t/l^2)_{1/2}]_a\}/\mathrm{d}(1/T),$$

where $[1/(t/l^2)_{1/2}]_a$ is the value of $1/(t/l^2)_{1/2}$ for absorption. Similarly, an apparent activation energy for desorption, E_d, may be defined. The values of E_a and E_d calculated from Fig. 8 are plotted as a function of temperature in Fig. 9. It is seen that E_a are greater than E_d in the temperature region studied.

For the system A-PS+ethyl acetate integral absorptions and desorptions from and to zero concentration were studied at 25°C in the same range of penetrant concentration as in the case of A-PS+benzene[13) and A-PS + ethyl methyl ketone.[7) The curves obtained had exactly the same features as those for A-PS+benzene mentioned above. Figure 10 gives the plots of $\log_{10}[1/(t/l^2)_{1/2}]$ vs. C_f for A-PS+ethyl acetate at 25°C. For the sake of comparison, the data for the benzene system and the ethyl methyl ketone system at the same temperature are also illustrated in the figure. It is seen that the plots for ethyl acetate and ethyl methyl ketone are almost represented by a single curve. This suggests that the values of diffusion coefficient and its dependence upon penetrant concentration for A-PS+ethyl acetate are nearly the same as those for the system A-PS+ethyl methyl ketone.

Summary

The successive differential absorptions for the A-PS+benzene system at 25, 35, and 50°C change with the initial concentration according to the scheme: sigmoid type→pseudo-Fickian type→two-stage type→Fickian type. The last transition, from two-stage to Fickian types, occurs at a lower concentration as the temperature of the experiment is raised. The values of the critical concentration for this transition are well compared with those for glass transition of the system. The successive differential absorptions for the A-PS+ethyl acetate system change their type with the increase of initial concentration according to the scheme, which is typical of systems of amorphous polymer+organic vapor; that is, sigmoid→pseudo-Fickian→two-stage→pseudo-Fickian→Fickian. The critical concentration for the last transition becomes lower in the order benzene, ethyl methyl ketone, and ethyl acetate. For all systems investigated the second stage portion of the two-stage process shifts rapidly to the short time regions as the initial concentration of each step increases. For A-PS+benzene the dependence of the rate of this shift upon intial concentration is very similar at 25, 35, and 50°C. For A-PS + ethyl acetate the rate of the shift depends upon initial concentration in nearly the same manner as in the A-PS+benzene system and the A-PS+ethyl methyl ketone system.

The general features of integral absorptions for

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15) R. M. Barrer and G. Skirrow, *J. Polymer Sci.*, **3**, 549 (1948).
16) van Amerongen, ibid., **5**, 307 (1950).
17) M. J. Hayes and G. S. Park, *Trans. Faraday Soc.*, **51**, 1134 (1955).
18) H. Fujita, A. Kishimoto and K. Matsumoto, ibid., **56**, 424 (1960).

the A-PS+benzene system at 25, 35, and 50°C are very similar, and the absorption curves show a pronounced dependence on concentration. At 25 and 35°C the logarithmic correlation plots of the overall rate of absorption and final equilibrium concentration are linear at the medium and high values of equilibrium concentration, and at 50°C the plots are linear over a nearly entire range of concentration studied. An apparent activation energy for absorption is greater than that for desorption in the temperature region investigated. The general feature of integral absorptions for the A-PS+ethyl acetate system is very similar to those for benzene and ethyl methyl ketone systems, irrespective of the difference in the penetrant-polymer interaction among these systems. The dependence of absorption rate upon concentration is also similar in general character to that for benzene and ethyl methyl ketone systems.

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