Representation of Gas Solubility in Glassy Polymers by a Concentration–Temperature Superposition Principle

Y. Mi, S. Zhou, and S. A. Stern*

Department of Chemical Engineering and Materials Science, Syracuse University, Syracuse, New York 13244

Received March 5, 1990; Revised Manuscript Received October 29, 1990

ABSTRACT: A new relation is derived to express the dependence of gas solubility in polymers on pressure, under conditions where the polymers are significantly plasticized by the penetrant gases. This relation shows that, for such conditions, the solubility isotherms have an inflection point which indicates a change in the solution mechanism. At pressures below the inflection point the solubility isotherms exhibit the nonlinearity characteristic of the "dual-mode sorption" behavior of gases in glassy polymers. At higher pressures, by contrast, the solubility isotherms become linear, as observed for gases in "rubbery" polymers in the Henry's law limit. This transition is attributed to the fact that plasticizing penetrants can depress the glass transition temperature of penetrant/polymer systems to the temperature of the isotherms at sufficiently high concentrations. The new solubility relation describes satisfactorily the solubility isotherms for CO_2 in several glassy polymers reported by Chiou, Maeda, and Paul and by Kamiya et al. These investigators also suggested the above mechanism.

I. Introduction

The solubility of light gases in glassy polymers is commonly a nonlinear function of the penetrant gas pressure. The solubility is defined here as the concentration c of a gas dissolved in a polymer at a pressure p and temperature T under conditions of solution equilibrium. The solubility isotherms for such gas/polymer systems, i.e., the isothermal plots of c versus p, are characteristically concave to the pressure axis. The solubility of most gases in polymers decreases with increasing temperature. When the temperature is raised above the glass transition temperature, T_g, of the polymers, i.e., the polymers are in their "rubbery" state, the solubility isotherms become linear, which indicates that the solubility is within the Henry's law limit.

The above behavior is described very satisfactorily by a "dual-mode" sorption model.[1-10] Chiou, Maeda, and Paul[11,12] have made the interesting observation that the solubility isotherms for CO_2 in glassy PMMA/PVF_2 blends at 35 °C exhibit an *inflection point* at 10–15 atm, depending on the blend composition. Similar observations were made recently by Kamiya et al.,[13] who measured the solubility of CO_2 in glassy poly(vinyl benzoate) at 25, 35, and 45 °C and at elevated pressures. The solubility isotherms for these CO_2/polymer systems also exhibit an inflection point at specific pressures, which increase with decreasing temperature.

The solubility isotherms for the above CO_2/polymer systems at pressures (or penetrant concentrations in the polymers) *below* the inflection point are concave to the pressure axis and "history"-dependent. Such a solubility behavior has been observed with CO_2 in a variety of other glassy polymers and can be represented by the dual-mode sorption model.[1-10] However, at CO_2 pressures (or concentrations) *above* the inflection point the solubility isotherms are linear, as has been observed with CO_2 in many rubbery polymers.[6-8,14] The linear segments of the solubility isotherms extrapolate to the origin of these plots, indicating that the solubility of CO_2 obeys Henry's law above the inflection point.

The present study proposes a method of predicting the penetrant pressure (or concentration) at which solubility isotherms of gases in glassy polymers exhibit an inflection point and beyond which the isotherms become linear.

II. General Considerations

A. Interpretation of Inflections in Solubility Isotherms. Chiou, Maeda, and Paul[11,12] as well as Kamiya et al.[13] have suggested that the T_g of CO_2/polymer systems decreases with increasing CO_2 pressure (or concentration in the polymers). Moreover, at the penetrant pressure (or concentration) corresponding to the inflection point of a solubility isotherm, the T_g of the penetrant/polymer system is *depressed* to the experimental temperature of the isotherm. The polymer is then in the glassy state when the penetrant pressure (concentration) is lower than at the inflection point and in the rubbery state at higher pressures (or concentrations). This hypothesis is confirmed by measurements of the T_g of poly(methyl methacrylate) (PMMA) and its blends with poly(vinylidene fluoride) (PVF_2)[11,12] and by estimates of T_g as a function of penetrant concentration[15] based on a relation proposed by Chow.[16]

The above behavior can be attributed to the fact that glassy polymers are plasticized by CO_2 and by other penetrant gases that exhibit a sufficiently high solubility in the polymers. The segmental motion of the polymer chains is then enhanced, and the chain-relaxation times are decreased with increasing penetrant concentration, as was evidenced by ^{13}C NMR[17] and stress-relaxation[18] measurements. Therefore, the effect of an increase in the concentration of a plasticizing penetrant in a polymer is similar to the effect of an increase in *temperature.*

It was mentioned above that the solubility of most gases in glassy polymers (T_g constant) decreases with increasing temperature T, which is equivalent to a decrease in the temperature difference $T_g - T$. The above considerations suggest that $T_g - T$ can also decrease at constant T, when the T_g of the glassy polymer is depressed by a plasticizing penetrant. The solubility of the penetrant should then be lower compared to that in an unplasticized polymer at the same p and T. Furthermore, this relative decrease in the penetrant solubility should be larger the higher the penetrant concentration.

It is suggested in the following sections that the change in the shape of solubility isotherms in glassy polymers caused by the depression of T_g can be described by a tem-

---

[*] To whom correspondence should be addressed.

0024-9297/91/2224-2361$02.50/0

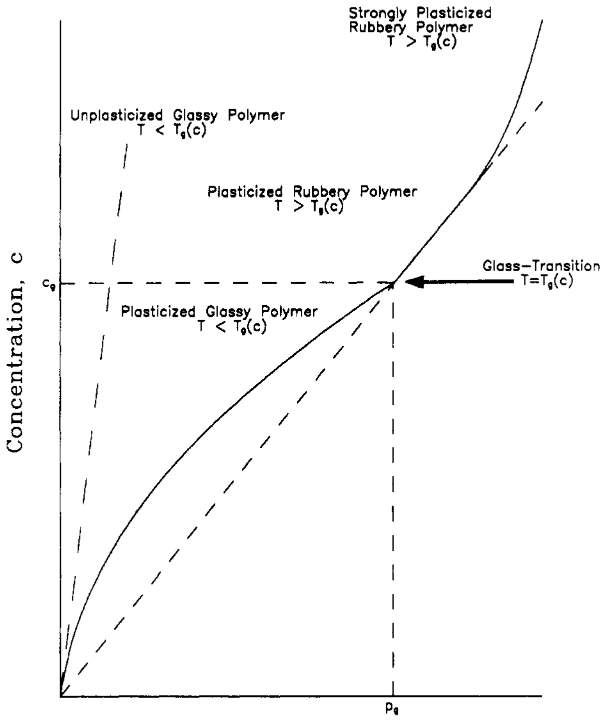

Figure 1. Typical solubility isotherms. All isotherms are for the same temperature.

perature–concentration "shift factor". This factor can be expressed quantitatively in terms of a modified Doolittle equation.

B. Solubility of Gases in Glassy Polymers. The following discussion will consider first the solution of a gas in glassy polymers under *hypothetical* conditions where the penetrant does not significantly plasticize the polymer; i.e., it does not affect the segmental motion of the polymer chains and the spectrum of chain-relaxation times. The penetrant concentration, c, can then be expressed as a function of the penetrant pressure, p, by Henry's law

$$c = S(0)\,p \tag{1}$$

where $S(0)$ is a solubility coefficient in the Henry's law limit; $S(0)$ depends only on the nature of the penetrant/polymer system and the temperature. Equation 1 is commonly valid at very low penetrant concentrations.

However, if the penetrant gas plasticizes the glassy polymer, the penetrant concentration c (the solubility) will be *lower* than in the hypothetical case mentioned above, at the same pressure and temperature. This lowering in solubility may be attributed to the factors described in the previous section. Therefore, eq 1 must be modified to the form

$$c = S(c)\,p \tag{2}$$

where $S(c)$ is a solubility coefficient which depends also on the penetrant concentration.

It is proposed to define a shift factor $\alpha_T(c)$ such that

$$S(c) = S(0)\,\alpha_T(c) \tag{3}$$

Equations 2 and 3 then yield the relation

$$c = S(0)\,\alpha_T(c)\,p \tag{4}$$

The shift factor $\alpha_T(c)$ decreases the value of the gas solubility in the hypothetical unplasticized polymer, given by Henry's law (eq 1), to that of the actual solubility in the plasticized polymer at a given pressure and temperature; cf. Figure 1.

It will be shown in the following section that $\alpha_T(c)$ can be defined in terms of a modified Doolittle equation[19] and that it can be related to the free volume of the penetrant/polymer system.

C. Concentration–Temperature Superposition Principle. 1. Modified Doolittle Equation. It is well-known from studies of polymer viscoelasticity that all relaxation times of polymers have the same temperature dependence.[19] Therefore, a temperature shift factor $\alpha_T(T)$ has been defined by the relation[19]

$$\alpha_T = \tau(T)/\tau(T_0) \tag{5}$$

where $\tau(T)$ is the time required to obtain a particular value of a given relaxation function (e.g., stress relaxation) at temperature T and $\tau(T_0)$ is the time required to obtain the *same* value of the relaxation function at an arbitrary reference temperature T_0. The temperature shift factor $\alpha_T(T)$ adjusts the time scale of a particular relaxation function from a temperature T to the reference temperature T_0.

The above shift factor is related to the mean fractional free volume of the polymer by the Doolittle equation[19,20]

$$\log \alpha_T(T) = \frac{B}{2.303}\left(\frac{1}{v_{\mathrm{f}}} - \frac{1}{v_{\mathrm{f}_0}}\right) \tag{6}$$

where v_{f} and v_{f_0} are the mean fractional free volumes of the polymer at temperatures T and T_0, respectively, and B is a characteristic constant.

Similarly, in cases where the polymer contains a dissolved penetrant (diluent), a concentration shift factor $\alpha_T(c)$ has been defined for isothermal conditions[19]

$$\alpha_T(c) = \tau(c_1)/\tau(c_2) \tag{7}$$

where $\tau(c_1)$ is the time required to obtain a particular value of a given relaxation function at penetrant concentration c_1 and $\tau(c_2)$ is the time required to obtain the same value of the relaxation function at a penetrant concentration c_2. A reference concentration is generally taken to be $c_2 = 0$.

It has been shown by Fujita[21,22] and by Ferry[23] that $\alpha_T(c)$ can also be related to the mean fractional free volume of a penetrant/polymer system by means of the Doolittle equation[19,20]

$$\log \alpha_T(c) = \frac{B^c}{2.303}\left(\frac{1}{v_{\mathrm{f}_c}} - \frac{1}{v_{\mathrm{f}_{c0}}}\right) \tag{8}$$

where v_{f_c} is the fractional free volume of the penetrant/polymer system at temperature T and concentration c; $v_{\mathrm{f}_{c0}}$ is the fractional free volume of the pure polymer ($c = 0$) at the same temperature; and B^c is a characteristic constant. For a given penetrant/polymer system and temperature, the shift factor $\alpha_T(c)$ is a function of the penetrant concentration only. Equation 8 was originally considered to be valid only in the temperature range of $T_g < T < T + 100$ °C, i.e., for the rubbery polymer state. Williams, Landel, and Ferry[20] as well as Matsuoka[24] have shown that eq 8 can also be applied in a suitably modified form to glassy polymers.

In the present study, a shift factor $\alpha_T(c)$ for the solubility of penetrant gases in glassy polymers is defined as

$$\log \alpha_T(c) = \frac{B^{s'}}{2.303}\left(\frac{1}{v_{\mathrm{f}_c}} - \frac{1}{v_{\mathrm{f}_{c0}}}\right)\frac{T_g(0) - T}{T_g(0) - T + \epsilon} \tag{9}$$

where $B^{s'}$ is a characteristic constant; T is the experimental temperature; $T_g(0)$ is the glass transition temperature of the pure polymer ($c = 0$); and ϵ is a finite but very small number that is required to avoid an undeterminate value of $\alpha_T(c)$ at $T = T_g(0)$. The term $[T_g(0) - T]/[T_g(0) - T + \epsilon]$ is introduced to make $\alpha_T(c)$ equal to unity at $T = T_g(0)$. T and $T_g(0)$ are absolute temperatures. The shift factor $\alpha_T(c)$ defined by eq 9 is used in eqs 3 and 4.

2. Free Volume and Glass Transition of Penetrant/Polymer Systems. The fractional free volume of a penetrant/polymer system, v_{f_c}, at a given temperature T can be expressed to a first approximation as a linear function of the penetrant weight-fraction, w, by the relation[19]

$$v_{f_w}(T,w) = v_{f_{w0}}(T) + \gamma' w \tag{10}$$

where $v_{f_w}(T,w)$ is the fractional free volume of the penetrant/polymer system at temperature T and a penetrant concentration w (in weight fraction); $v_{f_0}(T)$ is the fractional free volume of the pure polymer ($w = 0$); and γ' is a parameter.

Alternatively, eq 10 can be expressed in terms of the penetrant concentration c (e.g., in units of cubic centimeters (STP) or moles of penetrant per cubic centimeter of polymer)

$$v_{f_c}(T,c) = v_{f_{c0}}(T) + \gamma f(c) \tag{11}$$

where $v_{f_c}(T,c)$ and $v_{f_{c0}}(T)$ have been defined above, cf. eq 8; γ is a parameter that characterizes the concentration dependence of the penetrant/polymer system; and $f(c)$ is a function of c given by eq I-4 in Appendix I. With use of the technique of separation of variables, eq 11 can be rewritten in the form

$$v_{f_c}(T,c) = K(T)\, G(c) \tag{12}$$

where $K(T)$ is a function of temperature only, and $G(c)$ is a function of penetrant concentration only. In the most general case, $K(T)$ and $G(c)$ can take the form of polynomials. It is necessary to show that the difference between eq 11 and eq 12 is negligibly small. This can be demonstrated as follows.

$G(c)$ can be assumed for convenience to take the simpler form

$$G(c) = T_g(0)/T_g(c) \tag{13}$$

where $T_g(c)$ and $T_g(0)$ are the glass transition temperatures of the polymer containing a dissolved penetrant at concentration c and of the pure polymer ($c = 0$), respectively. $T_g(c)$ can be estimated from the relation proposed by Chow[16] (see Appendix I). $G(c)$ can be assumed to take the form given by eq 13, because $T_g(c)$ is a function of c only (see Appendix I), thus ensuring that $G(c)$ is a function of c only.

By substituting eq 13 into eq 12, one obtains

$$v_{f_c}(T,c) = K(T)\frac{T_g(0)}{T_g(c)} \tag{14}$$

It can then be shown that a function $K(T)$ can always be found such that the following inequality holds

$$\left|K(T)\frac{T_g(0)}{T_g(c)} - [v_{f_{c0}}(T) + \gamma f(c)]\right| < \epsilon^n \tag{15}$$

where ϵ is any given finite small number and n is a finite number. The magnitude of n depends on that of c. The above inequality ensures that the difference between eq 11 and eq 12 is negligible.[25]

3. Shift Factor $\alpha_T(c)$. By substituting eqs 11–13 into eq 9, one obtains

$$\log \alpha_T(c) = \frac{B^s T_g(c)}{2.303 v_{f_{c0}}(T)\, K(T)\, T_g(0)}[-\gamma f(c)][T_g(0) - T] \tag{16}$$

where $B^s = B^{s\prime}/[T_g(0) - T + \epsilon]$, and the other symbols are as used before.

As discussed previously, the T_g of a penetrant/polymer system decreases as the concentration of the penetrant in the polymer is increased. Hence, T_g can be expressed as a function of w by means of the relation[19]

$$T_g(w) = T_g(0) - kw \tag{17}$$

where k is a proportionality coefficient, which is approximately constant in the range $0 < w < 0.3$ for most penetrant/polymer systems. Equation 17 can also be expressed in terms of the concentration c

$$T_g(c) = T_g(0) - kf(c) \tag{18}$$

where the function $f(c)$ is the same as defined before.

It has been shown by Ferry that if the glass transition is an iso-free-volume state,[19] then $k = \gamma/\alpha_f$, where α_f is the difference in the coefficients of thermal expansion of the rubbery and glassy states of the polymer; substituting this relation into eq 18, one obtains

$$-\gamma f(c) = \alpha_f[T_g(c) - T_g(0)] \tag{19}$$

where all the symbols have the same significance as used previously.

By substitution of eq 19 into eq 16, the shift factor $\alpha_T(c)$ can then be expressed by the relation

$$\begin{aligned}\log \alpha_T(c) &= \frac{B^s \alpha_f}{2.303 v_{f_{c0}}(T)\, K(T)}\left[\frac{T_g(c)[T_g(c) - T_g(0)]}{T_g(0)}\right] \times \\ &[T_g(0) - T] = A\left[\frac{T_g(c)[T_g(c) - T_g(0)]}{[T_g(0)]^2}\right][T_g(0) - T]\end{aligned} \tag{20}$$

where

$$A = \frac{B^s \alpha_f T_g(0)}{2.303 v_{f_{c0}}(T)\, K(T)} \tag{21}$$

and where A is a parameter that depends only on the temperature and the nature of the penetrant/polymer system.

D. Solubility Isotherm for Plasticizing Penetrants. By substitution of eq 20 into eq 4, the following expression is obtained for the concentration c of a penetrant dissolved in a glassy polymer at pressure p and temperature T

$$c = S(0)\, p \exp\left\{A\left[\frac{T_g(c)[T_g(c) - T_g(0)][T_g(0) - T]}{[T_g(0)]^2}\right]\right\} \tag{22}$$

where all the symbols are as defined earlier. This equation contains two adjustable parameters, $S(0)$ and A, and should be useful in cases where a glassy polymer is plasticized by the penetrant. The glass transition temperature $T_g(0)$ of the pure polymer is generally known or can be measured, and $T_g(c)$ can be estimated from the relation of Chow;[16] cf. Appendix I.

Equation 22 has the following features, which are illustrated in Figure 1:

(1) It predicts that the solubility isotherm will be concave to the pressure axis in the pressure range $p < p_g$ (or when $c < c_g$). This behavior has been observed with many gases

Table I
Values of Parameters in Equation 22 for CO_2 in Poly(ethylene terephthalate)[a]

	parameters in eq 22		std dev[b]	
temp *t*, °C	*S*(0)	*A*	σ_1[c]	σ_2[d]
25	3.3340	0.6502	0.044 17	0.028 81
35	2.2366	0.7798	0.036 54	0.029 09
45	1.7664	1.0797	0.027 03	0.021 07
55	1.1356	1.1278	0.024 68	0.013 87
65	0.6929	1.4656	0.042 27	0.043 46
75	0.4569	1.7622	0.019 45	0.018 64
85	0.3331	5.0831	0.024 49	0.025 22

[a] Units: *S*(0), cm^3 (STP)/(cm^3 of polym atm); *A*, K^{-1}. [b] The standard deviation used is defined in Appendix II. [c] From eq 22. [d] From the dual-mode sorption model.

and vapors in a variety of glassy polymers and is accounted for in eq 22 by the fact that $T_g(c)$ is generally lower than $T_g(0)$ and decreases with increasing c. Hence, the exponential term in eq 22 is a decreasing function of c. In this pressure range alone ($p < p_g$), the dependence of the penetrant solubility on pressure is described by the dual-mode sorption model.[1-10]

(2) Equation 22 becomes linear at pressures $p > p_g$ where $T_g(c)$ is depressed to the temperature of the isotherm; i.e., $T_g(c) = T$. Equation 22 then reduces to

$$c = S(0)\, p \exp\left\{A\left[\frac{-T[T_g(0) - T]^2}{[T_g(0)]^2}\right]\right\} \tag{23}$$

Equation 23 is linear because the exponential term is a constant. Therefore, an inflection is introduced in the solubility isotherm.

The linear segment of the isotherms at $p > p_g$ may indicate that a further increase in penetrant concentration no longer increases the chain mobility and decreases the chain-relaxation times sufficiently to affect the gas solubility. In other words, the relaxation times are then shorter than the experimental time scale. This is the case for many light gases in *rubbery* polymers that are not significantly plasticized by the penetrant, i.e., when the gas solubility is within the Henry's law limit.

However, eq 22 should deviate from Henry's law and become *convex* to the pressure axis when the pressure is further increased, and the penetrant concentration becomes sufficiently high to plasticize the polymer, now in a rubbery state; cf. Figure 1.

(3) When $T_g(c) \rightarrow T_g(0)$, eq 22 approaches eq 1, which is linear and describes the dependence of c on p for a gas dissolved in a completely unplasticized glassy polymer.

III. Results and Discussion

A. Pressure Dependence of Solubility. The validity of eq 22 has been tested with a variety of experimental data reported in the literature, as is shown below. The data selected were those of Koros and Paul[26,27] for CO_2 in poly(ethylene terephthalate) (PET), of Chiou and Paul[12] for CO_2 in poly(vinylidene fluoride) (PVF_2) and poly(methyl methacrylate) (PMMA) blends, and of Kamiya et al.[13] for CO_2 in poly(vinyl benzoate) (PVB). The values of the parameters *S*(0) and *A* in eq 22 were obtained from nonlinear least-squares fits of eq 22 to the experimental data and are listed in Tables I and II.

Figure 2 presents the solubility isotherms for CO_2 in PET obtained by Koros and Paul[26,27] in the temperature range from 25 to 85 °C and at pressures from 1 to 20 atm. The symbols in Figure 2 represent the experimental data, whereas the solid curves are calculated from eq 22 in conjunction with the parameters *S*(0) and *A* listed in Table I. It can be seen that eq 22 suggests that the solubility isotherm at 85 °C has an inflection point at about 15 atm.

Table II
Values of Parameters in Equation 22 for CO_2 in Glassy Polymers[a]

		parameters in eq 22				
		absorption		desorption		
polymer[b]	temp *t*, °C	*S*(0)	*A*	*S*(0)	*A*	ref
PMMA/PVF_2 65/35	35	8.0715	0.2783	na	na	12
PMMA/PVF_2 50/50	35	2.0635	0.3987	na	na	12
PVB	25	9.2788	0.5070	6.6833	0.4352	13
	35	4.9687	0.7110	3.8809	0.6175	13
	45	3.4224	1.3440	3.0158	1.2610	13

polymer[c]	temp *t*, °C	$\bar{S}(0)$	$\bar{A}$	ref
PVB	35	4.311	0.6579	13
	45	3.362	1.3470	13

[a] Units: *S*(0), cm^3(STP)/(cm^3 of polym atm); *A*, K^{-1}. [b] PMMA/PVF_2 = polymer blends of poly(methyl methacrylate) and poly(vinylidene fluoride); PVB = poly(vinyl benzoate). [c] Mean values of parameters *S*(0) and *A* obtained from both adsorption and desorption measurements.

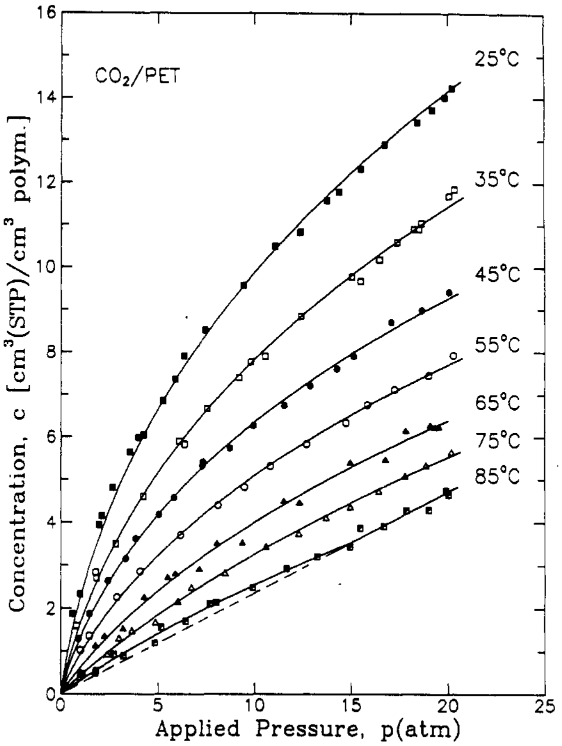

Figure 2. Solubility isotherms for CO_2 in poly(ethylene terephthalate) (PET) at several temperatures.[26,27] The solid curves drawn through the data points were calculated from eq 22 in conjunction with the parameters listed in Table I.

Also shown in Table I for comparison are the standard deviations for the fit of the dual-mode sorption model[1-10]

$$c = k_D p + \frac{c_H' b p}{1 + bp} \tag{24}$$

where k_D is a solubility coefficient in the Henry's law limit; c_H' is a "Langmuir capacity" constant; and b is a "Langmuir affinity" constant. In the standard form, c_H' is taken to be a function of temperature but independent of penetrant concentration. Clearly, the descriptions of sorption by eqs 22 and 24 are similar at higher temperatures as one approaches T_g. In fact, the two equations can be usefully considered as complementary rather than mutually exclusive descriptions of the nonequilibrium nature of the glassy state. For instance, if one equates eqs

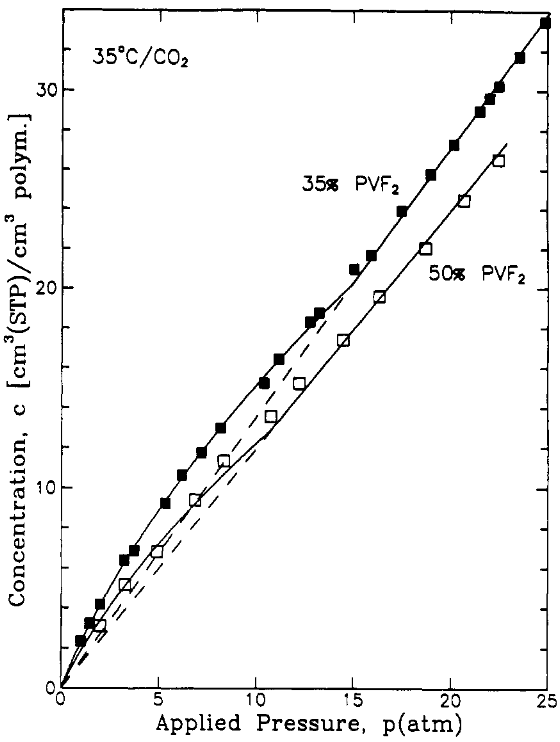

Figure 3. Solubility isotherms for CO_2 in 35% and 50% PVF_2/PMMA blends at 35 °C.[12] PVF_2 = poly(vinylidene fluoride); PMMA = poly(methyl methacrylate). The solid curves drawn through the data points were calculated from eq 22 in conjunction with the parameters listed in Table II.

22 and 24, it is clear that at constant temperature

$$S(0) = k_D + c_H'b \tag{25}$$

and

$$c_H' = \frac{k_D}{b}\,\frac{1 - \exp[F(c)]}{\exp[F(c)] - (1 + bp)^{-1}} \tag{26}$$

where

$$F(c) = A\left[\frac{T_g(c)[T_g(c) - T_g(0)]}{[T_g(0)]^2}\right][T_g(0) - T] \tag{27}$$

Equation 26 suggests that the c_H' expression, which is usually taken to be a constant at a fixed temperature, may be alternatively interpreted according to the treatment described here as a pressure- or concentration-dependent parameter. The functional form of this dependence of c_H' on p is known through the modified WLF expression for the concentration-induced depression in T_g discussed earlier.

Figures 3 and 4 show solubility isotherms for CO_2 in PMMA/PVF_2 blends obtained by Chiou and Paul[12] at 35 °C and at pressures up to 25 atm, and for CO_2 in PVB obtained by Kamiya et al.[13] in the temperature range from 25 to 45 °C and at pressures up to 50 atm. These data were interpreted by each of the two groups of authors in terms of two different modified forms of the original dual-mode sorption model; cf. eq 24. The parameters $S(0)$ and A for these systems are listed in Table II. The data in Figures 3 and 4 were obtained by digitizing the figures in the corresponding references using a CALCOMP Model 9100 digitizer connected to a Model 3200 SUN work station. These figures show that eq 22 describes successfully also the above solubility data. Standard deviations for the above data are not reported because these data were digitized.

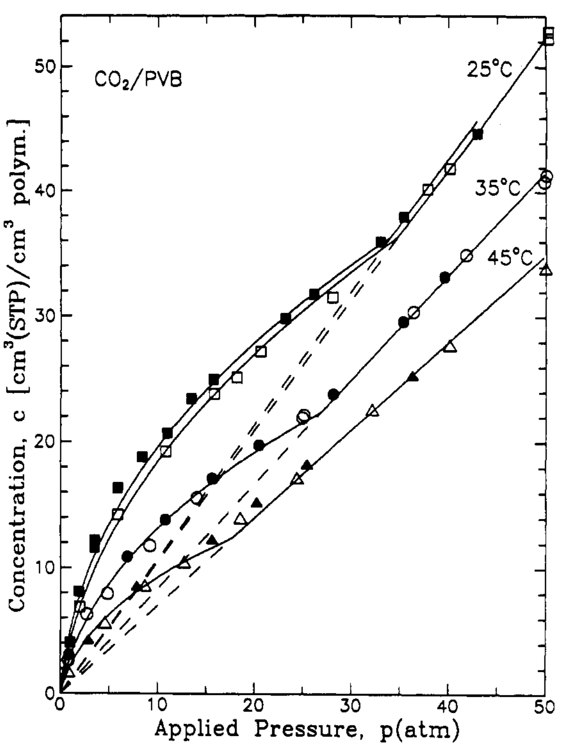

Figure 4. Solubility isotherms for CO_2 in poly(vinyl benzoate) (PVB) at 25, 35, and 45 °C. Open and filled symbols represent absorption and desorption, respectively.[13] The solid curves drawn through the data points were calculated from eq 22 in conjunction with the parameters listed in Table II.

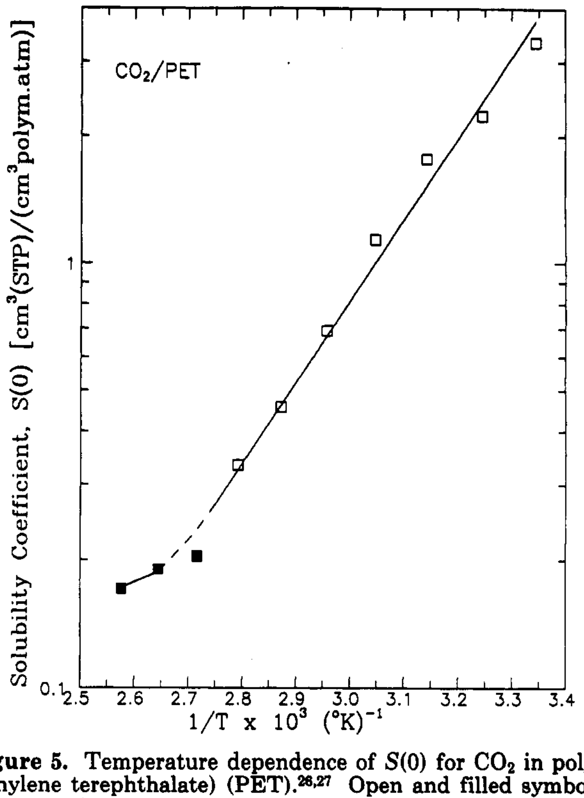

Figure 5. Temperature dependence of $S(0)$ for CO_2 in poly(ethylene terephthalate) (PET).[26,27] Open and filled symbols represent the temperature below and above T_g, respectively.[13]

B. Temperature Dependence of Parameters $S(0)$ and A. The parameter $S(0)$ is the solubility coefficient in the limit of zero concentration. Therefore, a van't Hoff type plot of log $S(0)$ versus $1/T$, the reciprocal absolute temperature, should be linear. Figure 5 shows that such a plot for CO_2 in PET[26,27] is indeed linear for both the glassy and rubbery states. The plot exhibits the usual

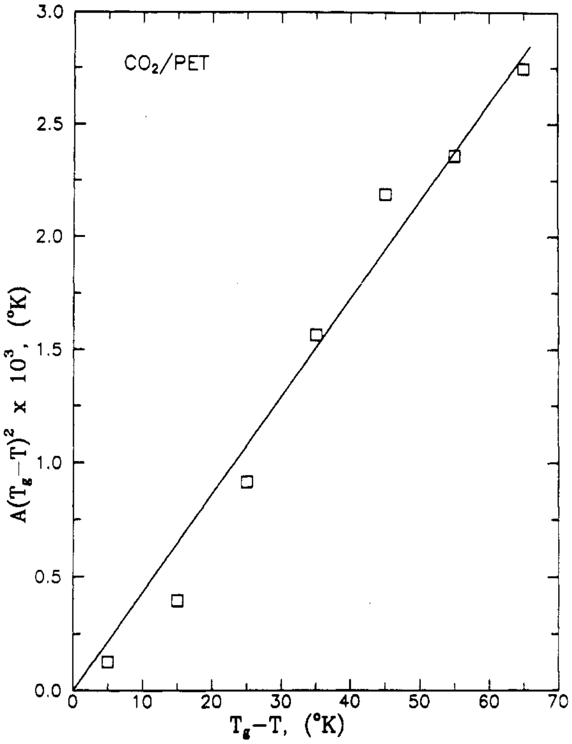

Figure 6. Temperature dependence of parameter A for CO_2 in poly(ethylene terephthalate) (PET).[26,27]

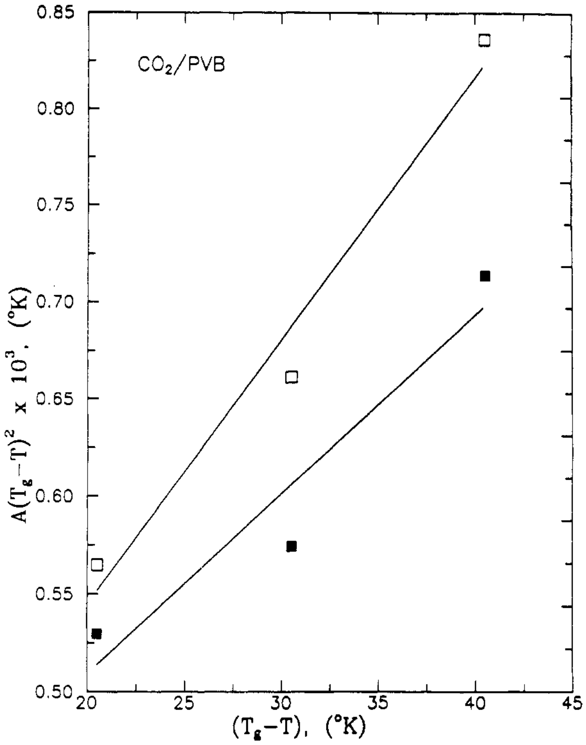

Figure 7. Temperature dependence of parameter A for CO_2 in poly(vinyl benzoate) (PVB).[13]

change in slope at the glass transition of the polymer, the slope being steeper below T_g than above for reasons discussed elsewhere.[28,29] The change in slope is gradual rather than discontinuous because the glass transition usually spans a temperature range of several degrees. The apparent enthalpies of solution obtained from the slopes of the above plots are −2.47 and −8.79 kcal/mol at temperatures above and below T_g, respectively.

Parameter A was found to increase with increasing temperature; cf. Tables I and II. A plot of $A[T_g(0) - T]^2$ versus $T_g(0) - T$ for CO_2 in PET was found to be linear; cf. Figure 6. The solid line in Figure 6 is a least-squares line that passes through the origin. Therefore, A is inversely proportional to $T_g(0) - T$. The same temperature dependence of A was also found for the absorption and desorption of CO_2 in PVB; cf. Figure 7.

Given eq 21, the temperature dependence of A is mainly due to the temperature dependence of B^s and $K(T)$. B^s is, by definition, inversely proportional to $T_g(0) - T$; cf. eqs 9 and 15. The temperature dependence of the function $K(T)$ is more complex. However, since parameter A is also inversely proportional to $T_g(0) - T$, $K(T)$ can only be a weak function of temperature as compared with B^s.

IV. Conclusions

Equation 22 represents satisfactorily the solubility c of a *plasticizing* penetrant in a glassy polymer as a function of the penetrant pressure p over a wide range of pressures (or penetrant concentrations). The equation represents all the features of c versus p plots observed experimentally: (a) the concavity of the plots with respect to the pressure axis at lower pressures, which is well described by the dual-mode sorption model;[1-10] (b) the inflection point in the plots at higher penetrant pressures (or concentrations); and (c) the linearity of the plots at pressures (or concentrations) above the inflection point, where the polymer is in the rubbery state. It is expected that positive deviations from linearity will be observed when the penetrant concentration in the rubbery polymer becomes sufficiently large. Equation 22 can be modified to take into acount also this behavior. Equation 22 contains two parameters, $S(0)$ and A, which can be estimated by the methods proposed in Appendix II.

The present analysis extends the original dual-mode sorption analysis (eq 24) to provide an alternative treatment for the reduction in the nonequilibrium nature of the polymer glass as T_g is approached. Both temperature-induced and concentration-induced changes in the nonequilibrium nature can be treated by using the present model.

It should be noted that the present study assumes that the free volume of the penetrant/polymer system is additive, as implied by eq 10. Therefore, the analysis will not apply to systems where this condition is not satisfied, for example, in cases where the penetrant forms molecular clusters.

The present treatment can also be used to describe the concentration dependence of the permeability and diffusion coefficients of plasticizing gases in glassy polymers. These extensions will be reported elsewhere.

Acknowledgment. The financial assistance of the U.S. Department of Energy, through its Office of Basic Energy Sciences, is gratefully acknowledged. Comments by Dr. R. L. Gordon have also been appreciated.

Appendix I. Calculation of $T_g(w)$

The glass transition temperature, $T_g(w)$, of a polymer containing a dissolved penetrant of weight fraction, w, can be estimated from the relation proposed by Chow:[16]

$$\ln\left(\frac{T_g(w)}{T_g(0)}\right) = \beta[(1-\theta)\ln(1-\theta) + \theta\ln\theta] \qquad \text{(I-1)}$$

The parameters β and θ are defined as

$$\beta = ZR/M_p\Delta C_p \qquad \text{(I-2)}$$

and

$$\theta = \frac{M_p}{ZM_d}\left[\frac{w}{1-w}\right] \qquad \text{(I-3)}$$

where Z is a lattice coordinate number which depends on the molecular weight (or size) of the penetrant and of the polymer repeating unit; Z is generally equal to 1 or 2; R is the universal gas constant; ΔC_p is the change in the heat capacity of the polymer at the glass transition; and M_p and M_d are the molecular weights of the polymer repeating unit and of the penetrant, respectively.

The penetrant weight fraction, w, and concentration, c, are related by the expression

$$w = \frac{M_d\frac{c}{22414}}{M_d\frac{c}{22412} + \rho_p} = f(c) \qquad \text{(I-4)}$$

where ρ_p is the density of the polymer in grams per cubic centimeters; 22 414 represents the volume, in cubic centimeters, of 1 mol of penetrant at STP; and M_d is the molecular weight of the penetrant. This relation assumes that the excess volume of mixing of the penetrant/polymer system is negligible.

Appendix II. Estimation of $S(0)$ and A

The estimation of parameters $S(0)$ and A in eq 22 was accomplished by a nonlinear least-squares regression method, which minimizes the squares-residual R^2

$$R^2 = \sum_1^N (c_i - c_{i,\mathrm{exptl}})^2 \qquad \text{(II-1)}$$

where c_i is the solubility calculated from eq 22 or from another suitable equation, and $c_{i,\mathrm{exptl}}$ is the experimental solubility.

The values of the parameters $S(0)$ and A obtained for several CO_2/polymer systems are listed in Tables I and II.

The standard deviation for the present model is defined by the relation

$$\sigma = [R^2/(N-2)] \qquad \text{(II-2)}$$

where R^2 is given by eq II-1, and the term c_i in eq II-1 is given by eq 22. Similarly, the standard deviation for the dual-mode sorption model is defined as

$$\sigma = [R^2/(N-3)] \qquad \text{(III-3)}$$

where R^2 is also given by eq II-1, and the term c_i in eq II-1 is calculated according to the dual-mode sorption model.

References and Notes

(1) Paul, D. R. *J. Polym. Sci., Polym. Phys. Ed.* **1969**, *7*, 1811–1818.
(2) Petropoulos, J. H. *J. Polym. Sci., Polym. Phys. Ed.* **1970**, *8*, 1797–1801.
(3) Paul, D. R.; Koros, W. J. *J. Polym. Sci., Polym. Phys. Ed.* **1976**, *14*, 675–685.
(4) Paul, D. R. *Ber. Bunsen-Ges. Phys. Chem.* **1979**, *83*, 294–302.
(5) Frisch, H. L. *Polym. Eng. Sci.* **1980**, *20*, 2–13.
(6) Stern, S. A.; Frisch, H. L. *Annu. Rev. Mater. Sci.* **1981**, *11*, 523–550.
(7) Frisch, H. L.; Stern, S. A. *Crit. Rev. Solid State Mater. Sci.* **1983**, *11* (2), 123–187.
(8) Koros, W. J.; Chern, R. T. In *Handbook of Separation Process Technology*; Rousseau, R. W., Ed.; Wiley-Interscience: New York, 1987; Chapter 20, pp 862–953.
(9) Vieth, W. R. *Membrane Systems: Analysis and Design*; Hanser Publishers: New York, 1988; pp 9–92.
(10) Stern, S. A.; Trohalaki, S. Fundamentals of Gas Diffusion in Rubbery and Glassy Polymers. *Barrier Polymers and Structures*; Koros, W. J., Ed.; ACS Symposium Series 423; American Chemical Society: Washington, DC, 1990, Chapter 2, pp 22–59.
(11) Chiou, J. S.; Maeda, Y.; Paul, D. R. *J. Appl. Polym. Sci.* **1984**, *30*, 4019–4029.
(12) Chiou, J. S.; Paul, D. R. *J. Appl. Polym. Sci.* **1986**, *32*, 2897–2918.
(13) Kamiya, Y.; Mizoguchi, K.; Naito, Y.; Hirose, T. *J. Polym. Sci., Part B: Polym. Phys.* **1986**, *24*, 535–547.
(14) Shah, V. M.; Hardy, B. J.; Stern, S. A. *J. Polym. Sci., Part B: Polym. Phys.* **1986**, *24*, 2033–2047.
(15) Chiou, J. S.; Barlow, J. W.; Paul, D. R. *J. Appl. Polym. Sci.* **1985**, *30*, 2633–2642.
(16) Chow, T. S. *Macromolecules* **1980**, *13*, 362–364.
(17) Raucher, D.; Sefcik, M. D. *Industrial Gas Separation*; Whyte, T. E., Jr., Yon, C. M., Wagener, E. H., Eds.; Washington, DC, 1982; pp 89–110.
(18) Heijboer, von J. *Kolloid-Z.* **1956**, *148*, 36–47.
(19) On the broad subject of modified Doolittle equations, the reader is referred to: Ferry, J. D. *Viscoelastic Properties of Polymers*; 3rd ed.; John Wiley and Sons: New York, 1980.
(20) Williams, M. L.; Landel, R. F.; Ferry, J. D. *J. Am. Chem. Soc.* **1955**, *77*, 3701–3707.
(21) Fujita, H.; Kishimoto, A. *J. Polym. Sci.* **1958**, *28*, 547–567.
(22) Fujita, H.; Kishimoto, A. *J. Chem. Phys.* **1961**, *34*, 393–398.
(23) Ferry, J. D.; Stratton, R. A. *Kolloid-Z.* **1960**, *171*, 107–111.
(24) Matsuoka, S. *Polym. Eng. Sci.* **1981**, *21*, 907–921.
(25) Feinerman, R. P.; Newman, D. J. *Polynomial Approximation*; Waverly Press: Baltimore, MD, 1974; Chapter 8, pp 81–89.
(26) Koros, W. J. Ph.D. Dissertation, Department of Chemical Engineering, The University of Texas at Austin, 1977.
(27) Koros, W. J.; Paul, D. R. *J. Polym. Sci., Polym. Phys. Ed.* **1978**, *16*, 1947–1963.
(28) Koros, W. J.; Paul, D. R.; Huvard, G. S. *Polymer* **1979**, *20*, 956–960.
(29) van Krevelen, D. W.; Hoftyzer, P. H. *Properties of Polymers, Their Estimation and Correlation with Chemical Structure*, 2nd ed.; Elsevier Scientific: New York, 1976.