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Notes

Continuous-Site Model for Langmuir Gas Sorption in Glassy Polymers

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Gas Sorption in Glassy Polymers

Gas sorption in glassy polymers is often analyzed in terms of an equation based on the assumption that diffusion in the polymer can be modeled in terms of a dual-mode picture in which the concentration is related to the pressure by two distinct mechanisms. The basic model was first suggested by Barrer et al.[1] and has been applied successfully to the analysis of data on a number of physical stems.[2-4] Transport models accounting for nonlinear effects produced by the dual-mode mechanism have been developed for permeability, time lags, and diffusion constants.[5-7] Let $C(p)$ be the total concentration of gas in the polymer in cm^3 (STP)/cm^3 polymer at a partial pressure, p (atm), of the penetrant in the gas phase. This concentration may be decomposed as $C(p) = C_D + C_H$, where C_D is the concentration of dissolved gas, and C_H the concentration of gas trapped in holes. The important feature of the dual-mode model consists of a choice of different isotherms for these two contributions. Specifically, it is generally assumed that the dissolved gas can be characterized by a Henry's law isotherm, $C_D = k_D p$, where k_D is Henry's law constant in cm^3 (STP)/cm^3 polymer atm and the concentration of gas in the holes can be represented by a Langmuir isotherm, $C_H = (C'_H \lambda p)/(1 + \lambda p)$, where C'_H is the Langmuir gas capacity in cm^3 (STP)/cm^3 polymer due to hole adsorption and λ is the Langmuir affinity constant in atm^{-1}. The resulting equation that relates concentration to pressure is

$$C(p) = k_D p + (C'_H \lambda p)/(1 + \lambda p) \qquad (1)$$

There are a number of shortcomings of the dual mode model represented by eq 1. The first is a restriction to exactly two kinds of gas sites. It is natural to suppose that a glassy polymer possesses a spectrum of site geometries and interaction energies that depend on temperature, pressure, thermal history, and other variables known to influence glass properties generally. A second shortcoming is that eq 1 does not predict saturation at sufficiently high pressures, suggesting that the Henry's law term should really be replaced by a second Langmuir isotherm.[8]

A more serious concern, however, is the correctness of the hypothesis that gas sorption represented mathematically by the Langmuir term has as its physical origin condensation and localization of gas molecules in preexisting voids in the glassy polymer. Several facts suggest that current understanding is incomplete and can be improved: (a) a van't Hoff plot of CO_2 solubility in glassy polycarbonate above room temperature[9] yields a slope corresponding to a solution exotherm of greater than 6 kcals/mol, far in excess of the heat of condensation of CO_2 at −50 °C (3.3 kcal/mol), and certainly quite remarkable for a gas above its critical temperature; (b) the entropy of solution for the same CO_2/polycarbonate system is in good accord with Trouton's rule (~20 cal/mol deg), even though the hypothetical liquid state to which the gas has condensed is above its critical temperature; (c) a regular solution treatment of liquid CO_2 leads to an estimated solubility parameter of 6.0 (cal/mL)$^{1/2}$ [10] while polycarbonate's solubility parameter is 9.4 (cal/mL)$^{1/2}$.[11] This mismatch in cohesive energies should lead to a solubility lower than the ideal value predicted by Raoult's law, while the measured solubility at room temperature of CO_2 in polycarbonate is greater than 3 times this ideal value.

Clearly special interactions must take place between the gas molecules and the polymer glass, and one clue is the unusually large entropy and partial molar volumes found when any (nonpolar) gas dissolves in a liquid. For example, the molar volume of N_2 at its boiling point is 34.7 cm^3/mol, while its partial molar volume in CCl_4 at 25 °C is 58.1 cm^3/mol. Comparison of a series of gas boiling point volumes with measured partial molar volumes in nonpolar liquids reveals that expansions of 35–55% are typical.[12] Jolly and Hildebrand attribute both effects to the "... increase in freedom of motion of the adjacent molecules of the solvent rather than to a change in the behavior of the gas molecule in a *cage*."[13] In a polymer glass, extra freedom of movement associated with neighbor gas molecules may be most important for polymer molecules frozen into highly strained, low-density states from the cooling through Tg. In the proximity of the gas, the strained polymer molecules can rearrange and begin to contract to the density of less strained neighbor regions which are nearer to equilibrium. Partially relaxing the glassy strains results in lower energy and better packing (i.e., lower volume). Such "gas-catalyzed annealing" of the polymer glass would explain the sorption behavior otherwise discussed in terms of the dual mode model of eq 1, but without requiring molecule-size voids and gas condensation.

This picture of gas molecules interacting with density fluctuations in the polymer glass suggests a different mathematical model of sorption from eq 1. A broad distribution of density fluctuation amplitudes is anticipated, and only a finite amount of relaxation (and therefore sorption) can occur for each. In the present note we propose a simple alternate to the dual mode which implicitly satisfies both requirements. The new model is phenomenological as is eq 1, and the latter may be regarded as a numerical approximation to a continuous distribution. A computational advantage of the new formulation is that it is able to fit polymer–gas data nearly as accurately as eq 1 using one less disposable parameter. The model is based on a single, continuous distribution of Langmuir

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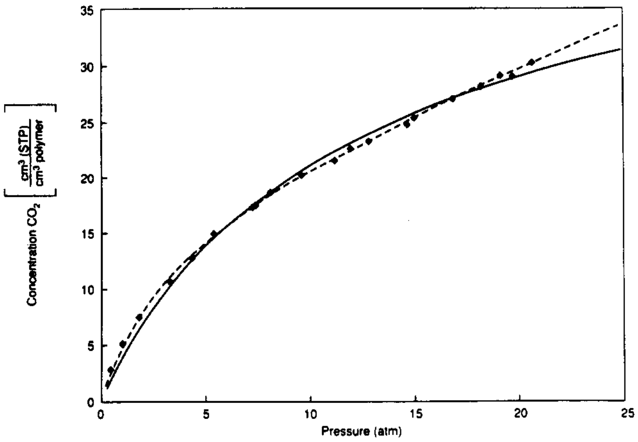

Figure 1. CO_2 sorption isotherm in polycarbonate at 35 °C: solid curve from eq 4a, with C_{max} = 52.7 cm^3 CO_2 (STP)/cm^3 polymer and a = 0.157 atm^{-1}; dashed curve from eq 1 with k_D = 0.685, C_H = 18.805, and λ = 0.262; parameters and data from ref 15 (Table A-1, p 219).

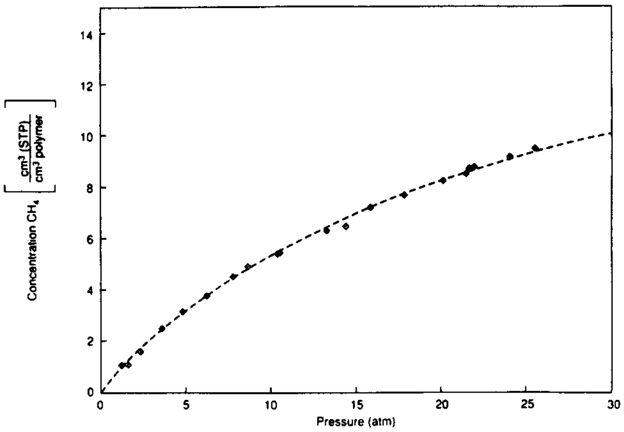

Figure 2. CH_4 sorption isotherm in polycarbonate at 35 °C: theoretical curve from eq 4a, with C_{max} = 21.25 cm^3 CH_4 (STP)/cm^3 polymer and a = 0.074 atm^{-1}; data from ref 15 (Table A-IV, p 222).

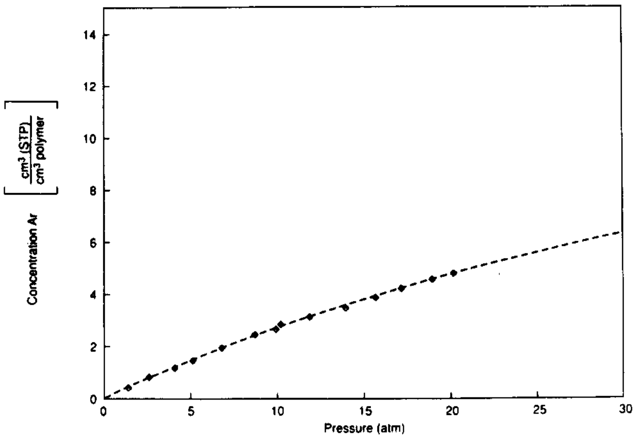

Figure 3. Ar sorption isotherm in polycarbonate at 35 °C: theoretical curve from eq 4a, with C_{max} = 22.85 cm^3 Ar (STP)/cm^3 polymer and a = 0.0284 atm^{-1}; data from ref 15 (Table A-IV, p 222).

isotherms expressed in terms of a distribution $\rho(\lambda)$ of affinity parameters λ (cf., eq 1). Here, however, we interpret a Langmuir site as an unrelaxed density fluctuation. The function $\rho(\lambda)$ is normalized in the sense that

$$\int_0^\infty \rho(\lambda)\,d\lambda = 1 \tag{2}$$

The concentration $C(p)$ is assumed to be expressible in terms of the pressure by the integral relation

$$C(p) = C_{sat}p \int_0^\infty \frac{\rho(\lambda)\lambda}{(1 + \lambda p)}\,d\lambda \tag{3}$$

where C_{sat} is the concentration at saturation.

It might seem that we have replaced the relatively simple relation in eq 1 by a much more complicated one, requiring that we find a function $\rho(\lambda)$ in place of the three parameters in the standard dual-mode isotherm. However, one expects on general mathematical grounds, that the value of the integral should be quite insensitive to the detailed form of $\rho(\lambda)$, which leads us to consider only very simple, specific forms of this function that allow evaluation of eq 3 explicitly, and which contain no more than a single parameter required to be determined from the data. We will show, by example, that good fits to data may be obtained with a number of simple choices of the function $\rho(\lambda)$.

We consider several possible one-parameter forms of $\rho(\lambda)$. (a) Constant $\rho(\lambda) = a^{-1}$ for $0 < \lambda < a$. Substituted into eq 3 this leads to

$$C(p) = C_{max}\left\{1 - \frac{\log(1 + ap)}{ap}\right\} \tag{4a}$$

(b) Linearly increasing $\rho(\lambda)$: $\rho(\lambda) = a\lambda$ for $0 < \lambda < \sqrt{2/a}$. Substituted into eq 3 this leads to

$$C(p) = C_{max}\left\{1 - \left\{\frac{\sqrt{2a}}{p} - \frac{a}{p^2}\log\left[\frac{p\sqrt{2a} + a}{a}\right]\right\}\right\} \tag{4b}$$

(c) Linearly decreasing $\rho(\lambda)$: $\rho(\lambda) = \sqrt{2a} - a\lambda$ for $0 < \lambda < \sqrt{2/a}$. Substituted into eq 3, this leads to

$$C(p) = C_{max}\left\{1 - \frac{1}{p^2}\left\{p\sqrt{2a}\left[\log\left[\frac{p\sqrt{2a} + a}{a}\right] - 1\right] + a\log\left[\frac{p\sqrt{2a} + a}{a}\right]\right\}\right\} \tag{4c}$$

(d) A fourth choice that allows λ to take on all possible values from 0 to ∞ and which still can be specified in terms of a single parameter is

$$\rho(\lambda) = p_0 e^{-p_0\lambda} \tag{4d}$$

where the average value of λ is equal to $1/p_0$. When this form for $\rho(\lambda)$ is substituted into eq 3 one finds

$$C(p) = C_{sat}\left[1 - \left(\frac{p_0}{p}\right)e^{p_0/p}E_1\left(\frac{p_0}{p}\right)\right] \tag{5}$$

where $E_1(x)$ is the exponential integral[14]

$$E_1(x) = \int_x^\infty \frac{e^{-t}}{t}\,dt$$

which has been tabulated. Easily programmed approximations to this function also are available.[14] Figures 1-4 show fits of sorption data[15] for CO_2, CH_4, Ar, and N_2 in polycarbonate at 35 °C fitted using the constant ρ model of eq 4a. Except for CO_2, the two-parameter fits using eq 4a are as good as the three-parameter *dual-mode* expression of eq 1.

Volume Effects

The interpretation of the Langmuir sites in eq 3 as density fluctuations able to contract upon interaction with gas molecules suggests that the partial molar volume of the sorbed gas will vary according to the size and amplitude of the polymer fluctuation it visits. One could roughly account for this variation of mixing volumes by assuming a linear dependence of the volume contraction with affinity parameter λ:

$$V_{CO_2}(\lambda) = V^0_{CO_2}(1 - b\lambda) \qquad (6)$$

A choice of $b = 3.0$ atm in eq 6 produces a good fit to the volume contraction results found by Fleming and Koros for CO_2 dissolved in polycarbonate.[16] A microscopic model is necessary to estimate the parameters used in the present model, but it is clear that the main features of the experimental results are reproduced faithfully and simply.

Discussion

This note formulates a model for gas sorption in glassy polymers based on the notion of a continuous distribution of Langmuir site interaction parameters, rather than the classical two-site model that allows only a single type of Henry and a single type of Langmuir site. A new interpretation of the Langmuir sorption mechanism is presented which, by analogy with gas dissolution in nonpolar liquids, suggests that the small mass and kinetic energy of the gas molecule loosens the environment of the glass molecules and is able to promote relaxation of low-density-polymer fluctuations. This reformulation contains the possibility of saturation of the polymer, which is not the case for the dual-mode sorption model. The new model therefore breaks down at some (high) gas pressure corresponding to complete occupation of all available sites. Plasticization of the glass will take place at or near this pressure, and render both eqs 1 and 3 inapplicable in any event.

The key quantity in the present model is the distribution of Langmuir affinity parameters, $\rho(\lambda)$. Though it might seem of critical importance to know this function accurately, this difficulty is avoided since one requires only an *average* with respect to $\rho(\lambda)$. Averages are insensitive to the precise form of the underlying distribution, ρ. Thus we show that a number of sets of data can be fit quite accurately in terms of a uniform distribution of λ, which is characterized by a single parameter that must generally be determined from the data. Other choices of $\rho(\lambda)$ which are specified by a single free parameter also reproduce the data approximately as well as the uniform distribution. The two-site model which yields an expression of the type shown in eq 1 can be regarded as a (2,1) Padé approximation to the form of $C(p)$ given in eq 3, the parameters in eq 1 being expressible in terms of moments of $\rho(\lambda)$ and the pressure at saturation, C_{max}. If the nth moment of $\rho(\lambda)$ is denoted by μ_n, then a simple calculation allows the identification

$$\lambda = \frac{\mu_3}{\mu_2} \qquad C_H' = C_{max}\frac{\mu_2^{\,3}}{\mu_3^{\,2}} \qquad k_D = C_{max}\left\{\mu_1 - \frac{\mu_2^{\,2}}{\mu_3}\right\}$$

For example, when eq 4a is fitted to sorption data[15] for N_2 in polycarbonate at 35 °C, one finds $C_{max} = 14.15$ cm^3 N_2 (STP)/cm^3 polymer and $a = 0.028$ atm^{-1}. When these values are used in the above expressions one finds $\lambda = 0.021$ atm^{-1}, $C_H' = 8.385$ cm^3 N_2 (STP)/cm^3 polymer, and $k_D = 0.022$ cm^3 N_2 (STP)/cm^3 polymer atm. Though these values differ from the dual-mode parameters used in ref 15, they also provide a very good fit to the experimental data.

The assertion that results are insensitive to the form of $\rho(\lambda)$ follows from the fact that there are many distributions having the same first three moments. It is clear, therefore, that on the basis of sorption data alone one is unable to differentiate between different theoretical approaches. Gusev and Suter have recently derived a model for gas sorption which also invokes a distribution of Langmuir sites.[17] They use molecular modeling of the glassy polymer–gas system to evaluate a site distribution function for gas molecules. We are presently extending the continuous-site model of the present article to also examine time-dependent properties such as permeability and time lags.[18] While the fitting functions examined in this note all have one disposable parameter, it is easy to improve the fit to experimental data by enlarging the class of $\rho(\lambda)$. This remains to be done.

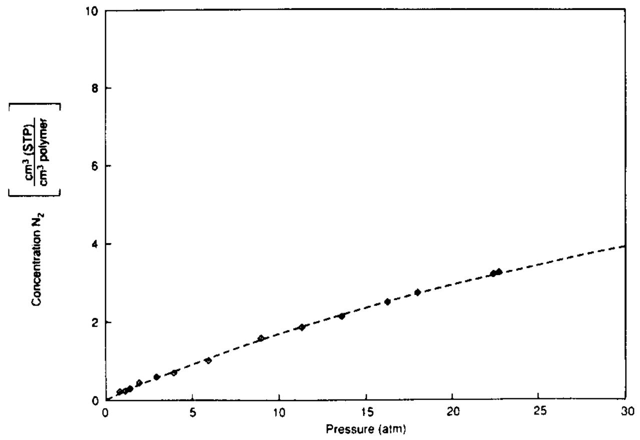

Figure 4. N_2 sorption isotherm in polycarbonate at 35 °C: theoretical curve from eq 4a, with $C_{max} = 14.15$ cm^3 N_2 (STP)/cm^3 polymer and $a = 0.028$ atm^{-1}; data from ref 15, (Table A-IV, p 222).

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Registry No. CO_2, 124-38-9; CH_4, 74-82-8; Ar, 7440-37-1; N_2, 7727-37-9.