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On the Sorption of Gases and Liquids in Glassy Polymers

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ABSTRACT: We present a thermodynamic theory of solubility of gases, vapors, and low-molecular-weight liquids in glassy polymers. We show that the distinctive features of sorption in glassy systems may be simply related to their elastic properties. As an illustration we analyze the data of vinyl chloride monomer absorption in poly(vinyl chloride) at various temperatures and vapor pressures and find a quantitative agreement with the model without any adjustable parameters.

Understanding the sorption of gases and liquids by plastics and elastomers seems to be important in many applications. Experimental data have been accumulated for more than 50 years. One of the most mysterious features of solvent sorption by polymers is a dramatic change of behavior when going from a molten to a glassy state (see, for example, refs 1–4 and references therein). First, in the glass the solubility increases strongly in a very nonlinear way when the partial pressure of the penetrant is increased. Second, in a glassy state at a given pressure, the solubility increases with decreasing temperature much faster than in a molten state. Such a behavior has often been interpreted in terms of an excess sorption of penetrant into specific sites (microvoids or holes) that are believed to exist only in a glassy state and disappear above the glass transition (the so-called dual-mode sorption models).

Recently, Vrentas and Vrentas have proposed a very interesting approach to analyze the sorption by glassy polymers without making reference to the existence of specific absorption sites.[5] They related the excess solvent uptake to the change of specific heat at the glass transition and to the change of glass transition temperature with penetrant concentration.

Another important progress in understanding the sorption of gases in glassy polymers without assuming absorption on some specific sites has been achieved by Lipscomb,[6] who has pointed out that the excess sorption can be related to the high bulk modulus of glasses. Lipscomb has characterized the glasses by some initial stress state but neglected its dependence on temperature and/or preparation conditions. Therefore, his model cannot fully account for the temperature dependence of sorption isotherms and in particular cannot describe situations in which the system undergoes a glassification transition due to desorption of a vapor.

Here, we present a complementary argument which enables us to address such situations and introduce a more complete picture of sorption behavior. Moreover, we find an interesting relation between the Vrentas and Vrentas[5] and Libpscomb[6] approaches since we show that the change of the specific heat at the glass transition (an essential parameter of Vrentas and Vrentas theory) is simply related to the stiffening of polymer at the glass transition.

The importance of elasticity can be illustrated by the following example of a cross-linked polymer (e.g., polystyrene) swollen by a vapor (e.g., toluene). In a dry state, our polymer network exists in the glassy state, whereas at high partial pressure it is osmotically swollen by the vapor molecules and is in a gellike state. The penetrant (vapor) concentration is determined by polymer–vapor effective interactions and cross-linking density. When the partial pressure p is decreased, the network deswells and the polymer volume fraction ϕ increases (Figure 1a). At a certain polymer concentration $\phi_g(T)$ the system becomes glassy. One of the essential features of this rubber to glass transition is a sharp increase of elastic moduli (Figure 1b). Further deswelling by a decrease of the vapor pressure is more difficult because our network became stiff and the shrinking is energetically costly. As a consequence the penetrant concentration varies little with partial pressure. Only at very low partial pressures can the network deswell to a dry state. It is well-known that to dry a network it is efficient to operate at temperatures above the glass transition temperature!

Before developing our thermodynamic theory we stress some important limitations of such an approach. Glassy polymers exhibit very slow relaxation processes and are not in a true thermal equilibrium state. As a result some of their properties may depend on thermal history. For example, the transition concentration $\phi_g(T)$ can somehow be displaced by annealing a glass for a long time. Therefore, our model cannot describe samples prepared under very different conditions, although some trends caused by annealing or physical aging can be anticipated if their influence on the glass transition temperature is known. For samples prepared under similar conditions many quantities (e.g., elastic moduli) can be treated as thermodynamic variables since they vary little on the time scale of sorption experiments.

Below we describe in more detail the proposed theory of glass osmosis. Consider a polymer which has reached an absorption equilibrium. For simplicity, we assume that the system is incompressible so that the state of the sample in absorption equilibrium is specified by (ϕ,T), with ϕ being the volume fraction and T being the temperature. Equilibrium is established when the chemical potential of penetrant molecules in a sample, $\mu(\phi,T)$, becomes equal to that in the surrounding gas or liquid phase, μ^{ext}. For incompressible systems, the chemical potential of the penetrant in the sample, $\mu(\phi,T)$, is related to the osmotic pressure $\pi(\phi,T)$ via the relation $\mu(\phi,T) = -\nu_1\pi(\phi,T)$. Indeed the addition of δN penetrant molecules to the sample

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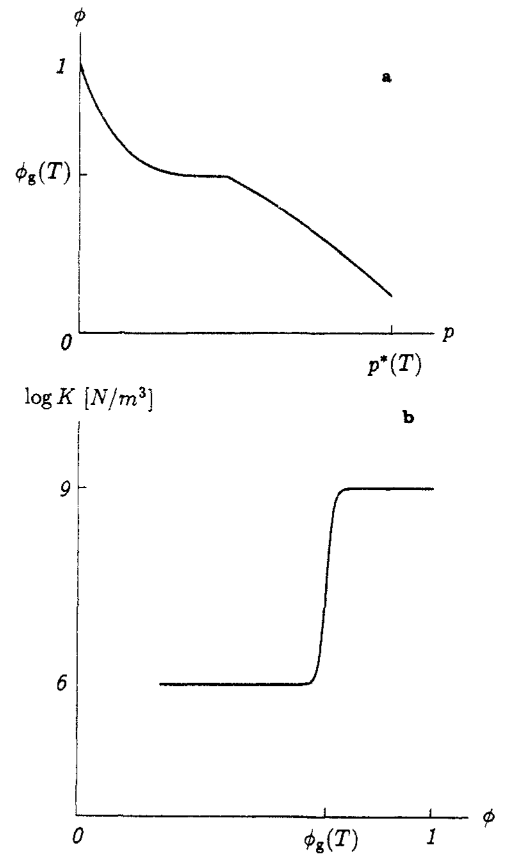

Figure 1. (a) Schematic representation of the sorption isotherm of a vapor–glassy polymer system. The polymer volume fraction ϕ is presented as a function of partial vapor pressure. $\phi_g(T)$ denotes a polymer volume fraction at which glass transition takes place; $p^*(T)$ is the saturated vapor pressure. (b) Schematic representation of the bulk modulus of a glassy polymer during deswelling. The logarithm of bulk modulus K is plotted versus the polymer volume fraction ϕ. At a polymer volume fraction $\phi_g(T)$ the polymer–penetrant system exhibits the glass transition and the modulus increases typically by a factor of 10^3.

amounts to the swelling of the sample by a volume $\delta V = \nu_1 \delta N$, and the work needed for this process is expressed either by $\mu \delta N$ or by $-\pi \delta V$. The bulk osmotic modulus $K(\phi,T)$ is equal to

$$K(\phi,T) = \phi \partial \pi(\phi,T)/\partial \phi \tag{1}$$

The integration of eq 1 with respect to ϕ at a fixed temperature yields

$$\pi(\phi,T) = \pi(\phi_0,T) + \int_{\phi_0}^{\phi} d\phi' \frac{K(\phi',T)}{\phi'} \tag{2}$$

One can measure the bulk modulus $K(\phi,T)$ by elastic deformation of the sample while allowing for the exchange of penetrant molecules between the sample and its surroundings. From such data one could in principle use eq 2 to find the chemical potential and the equilibrium sorption at various conditions. As we have already mentioned the important feature of the bulk modulus is its abrupt change around the glass transition (Figure 1b). At the glass transition one goes from the entropy to the elasticity-dominated regime in eq 2.

At a highly swollen state ($\phi < \phi_g(T)$) the system is in the gellike state and the osmotic pressure π can be calculated from the classical theories of polymer solution or gels in terms of the polymer–solvent interaction parameter χ or cross-linking density. For example, when the penetrant is a poor solvent, one can use the Flory–Huggins expression[7]

$$\pi(\phi,T) \simeq \pi_0(\phi,T) = -\frac{k_B T}{\nu_1}\{\log(1-\phi) + \phi + \chi\phi^2\} \tag{3}$$

For the deswollen systems in a glassy state ($\phi > \phi_g(T)$), it is a good approximation to write eq 2 as

$$\pi(\phi,T) = \pi_0(\phi,T) + \int_{\phi_g(T)}^{\phi} d\phi' \frac{K_{gl}(\phi',T)}{\phi'} \tag{4}$$

In eq 4, K_{gl} denotes additional contributions to the bulk modulus which result from the stiffening of the system at the glass transition. It is important to note that we can treat K_{gl} as a thermodynamic quantity, because the relaxation time of penetrant absorption is finite in a glassy state, while the relaxation time of the glassy state itself is practically infinite.

In practice, for a given glassy polymer K_{gl} changes little with the polymer volume fraction ϕ. Therefore, we simply replace $K_{gl}(\phi,T)$ by its value in a dry state, K_{gl}^0. Then, we can write the chemical potential of the penetrant inside the glass as

$$\mu(\phi,T) = k_B T\{\log(1-\phi) + \phi + \chi\phi^2\} - \nu_1 K_{gl}^0 \log \frac{\phi}{\phi_g(T)} \tag{5}$$

and calculate the absorbed solvent fraction, $1 - \phi$, by equating this chemical potential with μ^{ext}. The last term on the right-hand side of eq 5 represents a central result of the present work. This elastic contribution is at the very origin of the unusual sorption behavior of glasses.

Let us consider first the absorption from the vapor phase with partial pressure p below the saturated vapor pressure $p^*(T)$. Then the external chemical potential can be approximated by $\mu^{ext} = k_B T \log[p/p^*(T)]$. From eq 5 we get the absorption isotherm

$$p = p^*(T)\,(1-\phi)\exp\left\{\phi + \chi\phi^2 - \frac{\nu_1 K_{gl}^0}{k_B T}\log\frac{\phi}{\phi_g(T)}\right\} \tag{6}$$

which exhibits a strongly nonlinear behavior. It is interesting to remark that eq 6 has a structure which is analogous to an expression derived by Lipscomb (eq 21 of ref 6). The use of $\phi_g(T)$ in our formulation rather than of the stress at a reference pressure as in ref 6 enables us to treat more easily temperature effects and in particular to describe systems exhibiting glass transition during sorption.

For example, we now apply our formula to a typical situation, namely, the swelling of poly(vinyl chloride) (PVC) by vinyl chloride molecules (VCM). In Figure 2 we compare the theory with the data of Berens,[8] who studied both sorption isotherms and the change of the glass transition temperature with VCM concentration. We have taken $\chi \simeq 0.98$ as suggested by Berens and $K_{gl}^0 \simeq 1.1 \times 10^9$ N/m^2, a value typical to PVC. For such a highly swelling penetrant the agreement with the thermodynamic theory seems to be quite satisfactory.

In the low-pressure limit the solubility parameter S for eq 6 is equal to

$$S = \lim_{p\to 0}\,[(1-\phi)/p] = \frac{1}{p^*(T)}\exp\left\{-1 - \chi - \frac{\nu_1 K_{gl}^0}{k_B T}\log\phi_g(T)\right\} \tag{7}$$

Within the Flory–Huggins theory of sorption by melts above the glass transition temperature, the absorption isotherm is still given by eqs 5 and 6, but with $K_{gl}^0 = 0$. Hence, it is remarkable that the excess solubility of the

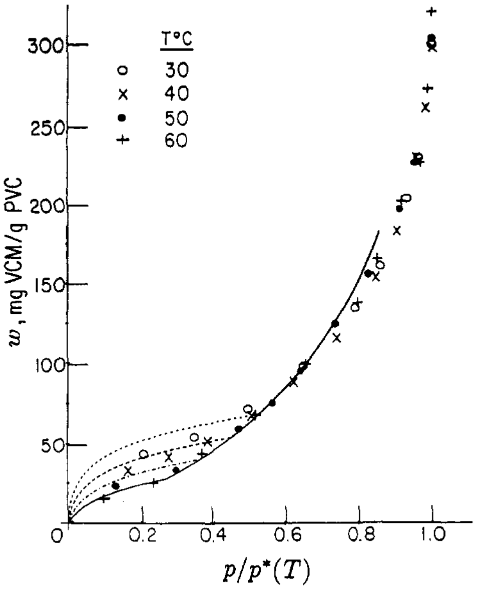

Figure 2. VCM solubility, w, in PVC as a function of $p/p^*(T)$. Points: experimental results from equilibrium vapor-pressure measurements by Berens.[8] Curves: calculated from eq 6 in the text with the temperatures $T = 30$ (dotted curve), 40 (dashed curve), 50 (dash-dotted curve), and 60 °C (solid curve).

vapor in the polymer in a glassy state is simply related to the existence of high elastic modulus K_{gl}^0 (eq 7) (cf. ref 6).

Consider the sorption of gases at temperature T above the liquid–gas critical temperature. The model predicts that the solubility coefficient S depends on the proximity of the glass transition of the polymer (see eq 7): $\log S \simeq -1 - \chi - (\nu_1 K_{gl}^0/k_B T) \log \phi_g(T) + C$, with constant C which depends only on gas and not a polymer and χ which characterizes polymer–gas interaction. It is difficult to know precisely $\phi_g(T)$ for such low swelling systems. We expect that for polymers which are closer to T_g (i.e., for $T_g - T$ low), one needs less penetrant to plasticize the glass, and $\phi_g(T)$ should be lower for systems with lower T_g. Therefore, at a given temperature polymers with lower glass transition temperature should absorb less than those with higher T_g. This seems indeed to be the case. For example, Barbari et al. have shown that the solubility of CO_2, CH_4, and N_2 at room temperature is lower in poly(hydroxy ether) ($T_g \simeq 94$ °C) than in poly(ether imide) which has $T_g \simeq 215$ °C.[9]

For a fixed temperature and at high temperatures eq 6 reduces to the form

$$p \simeq 1/S(1-\phi) \exp[\alpha(1-\phi)] \tag{8}$$

with $\alpha = -1 - 2\chi + \nu_1 K_{gl}^0/k_B T \simeq \nu_1 K_{gl}^0/k_B T$. It is interesting to note that eq 8 has the same form as the empirical relation proposed in the so-called gas–polymer-matrix model in which the exponential factor has been interpreted as arising from the variation of the gas–polymer interactions with penetrant concentration.[10] In our thermodynamic model the exponential factor α is simply related to the glass modulus K_{gl}^0: the stiffer the glass is, the stronger are the deviations from Henry's law. For very low swelling degrees ($\phi \simeq 1$) our model may overestimate somewhat the coefficient α because the penetration of solvent without appreciable change of volume seems possible. In principle, such effects of finite negative excess volume can be included in a thermodynamic approach.

It is interesting to remark that one can calculate the free energy $f(\phi,T)$ by integrating eq 5 for the chemical potential of penetrant $\mu = \partial(f/\phi)/\partial(1/\phi)$. One can derive then other thermodynamic quantities such as the specific heat $c_p = -T\partial^2 f/\partial T^2$. In particular, one finds a simple relation between the change of the specific heat Δc_p at the glass transition and the elastic modulus of a glass K_{gl}^0:

$$\Delta c_p \simeq K_{gl}^0\, T_g^0 \left(\frac{d\phi_g}{dT}\bigg|_{T_g^0}\right)^2 \tag{9}$$

where T_g^0 denotes the glass transition temperature of the dry polymer. Therefore, in principle, a description of the sorption of glassy polymers in terms of the elastic modulus or specific heat variation is deeply linked. Equation 9 seems to reproduce rather well the experimental data. For example, for a polycarbonate–carbon dioxide system eq 9 leads to $\Delta c_p \simeq 0.07$ cal/g·K (with $K_{gl}^0 \simeq 1.0 \times 10^9$ N/m^3 [11]), whereas the experimental value is 0.055 cal/g·K.[12]

In conclusion, we have shown that the excess sorption in a glassy polymer is simply related to the bulk modulus of the glass. From the measurements or estimations of the bulk modulus and concentration dependence of T_g one can calculate the absorption isotherms in the glassy state. The theory seems to work quantitatively for vapors and for gases. It seems to explain well the strong dependence of the solubility parameter on the distance from the glass transition temperature. However, it should be stressed that applying a thermodynamic approach needs some caution. Polymer glasses are not in a complete equilibrium and evolve on long time scales. Sample conditioning (history) may influence sorption behavior.[13,14] Therefore, a careful consideration of kinetic effects and a clear distinction between swelling and glass relaxation times would be very important. We hope that our picture may be of some relevance to understanding the diffusion of small molecules in glassy polymers and the anomalous kinetics of swelling.

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