Statistical Mechanics of "Dual-Mode" Sorption in Polyimides

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SYNOPSIS

A statistical mechanical description of the gas takeup or sorption in polyimides below their glass transition temperature is proposed. The model treated is formally similar to Fowler's early model of monolayer adsorption of gases on solid surfaces. It is expected to be appropriate for polymers exhibiting a significant degree of crystallization, e.g., the aromatic polyimides at temperatures well below their glass transition temperature. The model assumes that the penetrant gas molecules bind to a spectrum of states characterized by a distribution of binding energies. If it is assumed that the penetrant molecules bind to the polymer with only two well-defined interaction energies, namely, zero as well as some particular finite value, a "dual-mode" expression for sorption is obtained. It is pointed out that this "dual-mode" or "two-state" model is not consistent with some recent data obtained on carbon dioxide sorption in a polyimide. Two other simplified models are examined, a "uniform-density-of-states" model and a "three-state" model. The present treatment yields explicit expressions for the temperature dependence of the sorption parameters. This dependence reflects the thermodynamic redistribution of penetrant molecules among the available fixed density-of-states as the temperature is varied. It is pointed out that the temperature dependence of the Langmuir capacity constant obtained from nonlinear least squares fitting the standard "dual-mode" sorption expression to the polyimide sorption data may lead to an erroneous inference concerning the decrease in "unrelaxed volume" as the temperature is increased from well below the glass transition temperature of the polymer. The "three-state" model yields sorption isotherms that parallel the data of Sada et al. closely. This suggests the presence of multiple carbon dioxide binding sites in the polyimide. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

Polyimides have found widespread application as a result of their attractive mechanical, thermal, and electrical properties. Along with interest in microelectronics and aerospace applications, recent interest has also focused on the potential use of the high permselectivity of these materials in gas separation applications. As a result of this, a number of gas sorption and diffusion measurements have been performed.[1-7]

The interpretation of sorption and permeability in polymers has had an extensive history, which dates back to early investigations and analyses of gas sorption and permeability in the rubbery as well as the glassy state.[8-10] Below the glass transition temperature, in the "glassy state," the gas takeup or sorption as a function of the ambient gas pressure exhibits saturation not generally observed for rubbery materials. Such behavior has been interpreted in terms of a "dual-sorption" model which provides a macroscopic framework for description of the sorption as well as for the steady state permeability.[8-15] Whereas dual-sorption theory has provided expressions that allow one to fit the data, and to discuss the implications of solubility with respect to the steady state permeability of the polyimides, it has provided little contact with the microscopic mechanism or mechanisms that are responsible for the shape of the observed sorption and permeability coefficient isotherms.

The quasicrystalline nature of polyimides below their glass transition temperatures leads one to infer that statistical mechanical theories proposed in connection with the analysis of adsorption isotherms[16-24] could well be useful in describing the sorption isotherms of these materials. The relevance of such statistical mechanical interpretation of sorption phenomena in polymers had been pointed out in an early investigation.[9] Earlier investigations of the solubility of gases in elastomers,[25] a statistical mechanical theory of multimolecular absorption[26] and its application to wool,[27] have also suggested the relevance of such approach in treating sorption in glassy polymers.

Although it is true that structural relaxation in the vicinity of the glass transition will lead to complicating features not encountered in situations where molecular binding sites are fixed in energy and structure, well below the glass transition temperature one might expect "intrinsic" temperature dependences to prevail, i.e., those temperature dependences that arise from the thermodynamics of the ambient gas and the redistribution of molecules among a fixed density-of-states. In any event, a complete microscopic theory of sorption in glassy/crystalline polymers will ultimately require not only treatment of these "intrinsic" temperature dependent effects but "extrinsic" effects as well, i.e., those effects arising from structural changes induced by variations in temperature as well as by the sorbed gas concentration.

The present paper has been primarily motivated by the sorption measurements of Sada et al.[1] In what follows, we will derive an expression for the sorption at thermal equilibrium with the use of a simple statistical mechanical model of the gas takeup in a glassy/crystalline polymer. The set of assumptions that yield a dual-sorption isotherm will be examined. The present treatment yields explicit expressions for the temperature dependence of the dual-sorption parameters resulting from the thermodynamic redistribution of penetrant molecules among the available binding sites. Such derivation provides a basis for understanding certain of the limitations inherent in a dual-sorption interpretation of polyimide data. It will be pointed out that the data of Sada[1] is not consistent with the expected temperature dependences expected from a dual-sorption theory. It will be demonstrated, with use of a "three-state" model, that the temperature dependence of the Langmuir capacity constant, $C_{H'}$, obtained from nonlinear least squares fitting the standard dual-mode sorption expression to polyimide sorption data should be interpreted with caution. Inferences con-

cerning the decrease in "unrelaxed volume" of the polymer that depend upon this temperature dependence may not be correct. The three-state model does indeed provide sorption isotherms that parallel the observed sorption (Fig. 1 of Ref. 1) of carbon dioxide in the polyimide quite closely.

STATISTICAL MECHANICAL MODEL

The following development closely follows that of Fowler[28,29] as well as that of a number of other investigators who have adapted the Fowler treatment to localized molecular adsorption on the surface as well as sorption in the interior of solids.[21,22,24,26,27] We assume that the gas molecules are in thermal equilibrium with the polymer and that the polymer provides a distribution of binding sites for these molecules. This distribution is characterized by an energy density of binding states. We envisage a range of binding energies: from values of essentially zero electron volts to values of several tenths of electron volts. Implicit in the present derivation is the assumption that well below the glass transition temperature of the polyimides one can neglect structural relaxation as a function of gas take up.

For N_1 sites of binding energy E_1, N_2 sites of binding energy E_2, and so forth, the partition function of the gas–polymer system, Z, can be written as

$$Z = \frac{N_1!}{(N_1 - n_1)! \, n_1!} \frac{N_2!}{(N_2 - n_2)! \, n_2!} \cdots [a_1(T)]^{n_1} [a_2(T)]^{n_2} \cdots \quad (1)$$

We have assumed that n_1 of the gas molecules are distributed among the N_1 states of binding energy E_1, n_2 of the gas molecules distributed among the N_2 states of binding energy E_2, and so forth. Only one molecule is assumed to bind per site. The molecules are also assumed to be noninteracting with each other. $a_i(T)$, the partition function of the molecule bound to the ith type site, can be written as

$$a_i(T) = e^{E_i/KT} j_i(T) \quad (2)$$

The partition function for the internal degrees of freedom of the molecule, $j_i(T)$, has been factored to explicitly exhibit the shift in energy that arises from the binding of the gaseous molecule to the localized polymer site.

The absolute activity λ_i of the molecules bound at the i sites is written as

$$\lambda_i = \frac{1}{a_i(T)} \frac{\theta_i}{(1 - \theta_i)} \qquad (3)$$

where θ_i is the fractional occupation of the ith type site. The absolute activity λ_g of the molecules in the gaseous phase is given by

$$\lambda_g = \frac{p}{KT} \frac{h^3}{(2\pi mKT)^{3/2} j_g(T)} \qquad (4)$$

with p the ambient pressure.

Assuming equilibrium between the molecules in the gaseous phase and in the polymer, the fractional occupation of each set of binding states can be written as a function of the ambient pressure:

$$\theta_i = \frac{\alpha_i e^{\Delta_i} p}{1 + \alpha_i e^{\Delta_i} p} \qquad (5)$$

with

$$\alpha_i = \frac{j_i}{j_g} \frac{1}{KT} \frac{h^3}{(2\pi mKT)^{3/2}} \qquad (6)$$

and

$$\Delta_i = E_i / KT$$

The total gas takeup C in the polymer is then just given by

$$C = \sum_i n_i = \sum_i \frac{\alpha_i N_i e^{\Delta_i} p}{(1 + \alpha_i e^{\Delta_i} p)} \qquad (7)$$

or, for a continuous density of binding states $g(\epsilon)$,

$$C = \int_0^\infty \frac{g(\epsilon)\alpha(\epsilon)e^{\Delta(\epsilon)}p \, d\epsilon}{1 + \alpha(\epsilon)e^{\Delta(\epsilon)}p} \qquad (8)$$

Equation (8), the expression for the sorption isotherm, is composed of just a sum of Langmuir terms, each associated with a density-of-states $g(\epsilon)$ at binding energy ϵ. Consistent with the set of assumptions for this model, the total gas takeup in the polymer is given by a Fermi–Dirac distribution of molecules over states of energy ϵ with degeneracy $g(\epsilon)$. Such a model involves a number of simplifying assumptions and modification of these with respect to site occupancy number, nonvanishing molecular interaction energy, etc., will yield a different expression for the sorption isotherm. As stated previously, the present model has been previously proposed in connection with a number of other adsorption and sorption phenomena.

DUAL-MODE SORPTION: THE "TWO-STATE" MODEL

Examination of eq. (8) indicates that the numerical value of the factor $\alpha(\epsilon)e^{\Delta(\epsilon)}$ plays a crucial role in determining the onset of the nonlinearity, or saturation, of the sorption isotherm with pressure. This factor can be identified as a generalized Langmuir affinity constant for the set of states of energy ϵ. It involves fundamental constants, the ratio of partition functions of the internal degrees of freedom of the molecule, j_i / j_g, all of this modulated by the exponential factor. There has been previous discussion[22,25,26] of what might be expected for the value of this ratio of partition functions. One expects localization of the molecules to decrease the partition function for the internal degrees of freedom; however, consistent with the preliminary nature of the present discussion, we will, at present, assume this ratio of partition functions to be equal to unity. The parameter α is therefore independent of the particular binding site. It can then be evaluated for CO_2 at room temperature and is found to be 8.7 $\times 10^{-13}$ atm^{-1}. This sets a constraint on the binding energies required so that the onset of saturation is observed in the vicinity of one atmosphere of ambient gas pressure. Figure 1 shows a semilog plot of the product $\alpha e^{E/KT}$, at 30°C as a function of the energy, E. One notes that observation of the onset of saturation, in the vicinity of 1 atm, requires states with binding energies of several tenths of electron volts. States with binding energies that are significantly less, resulting in a factor small compared with
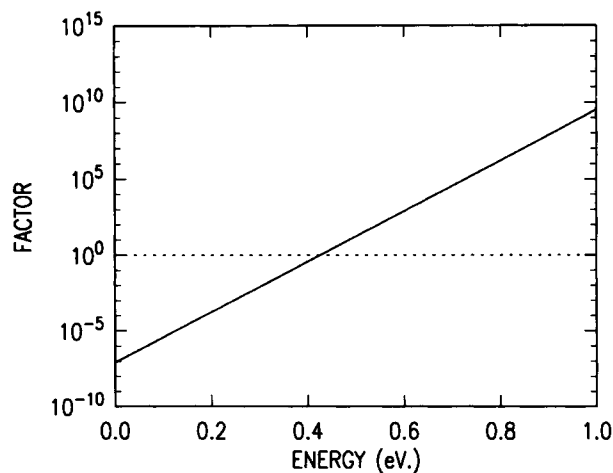
Figure 1   The factor $\alpha e^{\Delta(E)}$ as a function of polymer site binding energy E.

unity, will contribute Henry-type terms to the expression for the sorption isotherm, eq. (8).

In the remainder of this section we will assume that there are only two types of binding sites, one with essentially zero binding energy and one having a binding energy of tenths of an electron volt. If we neglect the pressure dependence in the denominator of the term associated with sorption for the states of either zero or negligible binding energy, the total sorption can be written as

$$C = G(0)\alpha p + G(E)\frac{\alpha e^{\Delta(E)}p}{1 + \alpha e^{\Delta(E)}p} \qquad (9)$$

$G(0)$ and $G(E)$ are the numbers of states with binding energy equal to zero, and equal to E, respectively. Equation (9) has just the functional form of the dual-sorption isotherm:

$$C = k_D p + \frac{C_{H'}bp}{1 + bp} \qquad (10)$$

with dual-sorption parameters given by

$$k_D = G(0)\alpha \qquad (11)$$

$$C_{H'} = G(E) \qquad (12)$$

$$b = \alpha e^{\Delta(E)} \qquad (13)$$

If at present we assume that $G(0)$ and $G(E)$ are temperature-independent, the temperature dependence of all three dual-sorption parameters is significantly different. At temperatures in the vicinity of room temperature, the Langmuir affinity constant b will be significantly temperature-dependent, exhibiting Arrhenius behavior. The Henry constant will vary as $t^{-5/2}$, and the Langmuir capacity constant, as assumed, will be independent of temperature. If this two-state or dual-sorption model, treating only "intrinsic" temperature dependent effects, well below the glass transition temperature, was appropriate in describing the sorption of CO_2 in the polyimides, then fitting several dual-sorption isotherms over a small range of temperatures near room temperature should yield a relatively temperature-independent Langmuir capacity constant. Sorption measurements of carbon dioxide in the polyimides,[1,4] on the other hand, yield a Langmuir capacity constant that decreases significantly over tens of degrees centigrade just above room temperature.

UNIFORM DENSITY-OF-STATES

In this section we examine the case for which the density-of-states is uniform up to some cutoff en-

ergy. In connection with this uniform-density-of-states model, the sorption isotherm resulting from such broad distribution of states will be compared with the dual-sorption isotherm. Certain limiting expressions for the sorption will also be examined. The purpose of the present section is to emphasize that differences in the shape of the sorption isotherm reflect differences in the distribution of molecular binding sites.

Let us assume that the density-of-states $g(\epsilon)$ in eq. (8) is uniform up to some cutoff energy E_0, past which it is zero:

$$g(\epsilon) = N_0 \quad 0 \le \epsilon \le E_0; \quad g(\epsilon) = 0 \quad \epsilon > E_0$$

Equation (8) is then simply integrable and the concentration C can then be written

$$C = N_0 KT \ln\left(\frac{1 + \alpha p e^{E_0/KT}}{1 + \alpha p}\right) \qquad (14)$$

At low pressures the concentration varies linearly with pressure:

$$C = N_0 KT \alpha p (e^{E_0/KT} - 1) \qquad (15)$$

At infinite pressure, all available sorption sites are filled

$$C = N_0 E_0 \qquad (16)$$

Between these limits, i.e., for $\alpha p \ll 1$ and $\alpha p e^{E_0/KT} \gg 1$ one can write:
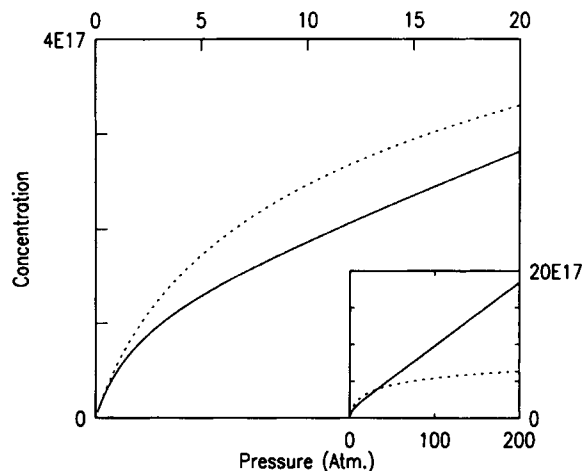
$$C = N_0 KT(E_0/KT + \ln(\alpha p))$$

Figure 2 Gas concentration (takeup) in the polymer as a function of pressure for the two-state (———) and "uniform density-of-states" (– – –) models.

Figure 2 shows sorption isotherms for the "two-state" (dual-sorption) and uniform density-of-states model at 25°C. A correspondence between the density-of-states of the two models has been made by fixing the initial linear increase in take-up to be the same for the two different models. It is of interest that over the range of accessible experimental pressures, the uniform density-of-states model exhibits greater takeup than the "two-state" or dual-sorption model. As shown in the inset of Figure 2, at higher pressures there is a crossover in take-up with the "two-state" model exhibiting greater sorption.

"THREE-STATE" MODEL AND THE LANGMUIR CAPACITY CONSTANT

Figure 3 shows sorption isotherms calculated at four temperatures just above room temperature for a "three-state" sorption model with gas takeup C given by

$$C = \alpha N_1 p + \frac{\alpha N_2 e^{\Delta_2} p}{1 + \alpha e^{\Delta_2} p} + \frac{\alpha N_3 e^{\Delta_3} p}{1 + \alpha e^{\Delta_3} p} \quad (17)$$

with $N_1 = 1E23$, $N_2 = 9.0E18$, $N_3 = 6.0E17$, $E_1 = 0.0$ eV, $E_2 = 0.32$ eV, and $E_3 = 0.45$ eV. The expression for α is given by eq. (6) with the ratio of partition functions taken equal to unity. Enhanced sorption at the lower temperatures reflects the increased occupation of molecules in the binding states of finite energy. Over a range of temperatures significantly below the glass transition temperature, i.e., over the range investigated for several of the polyimides, one therefore expects the redistribution of molecules among the binding sites to make a significant con-
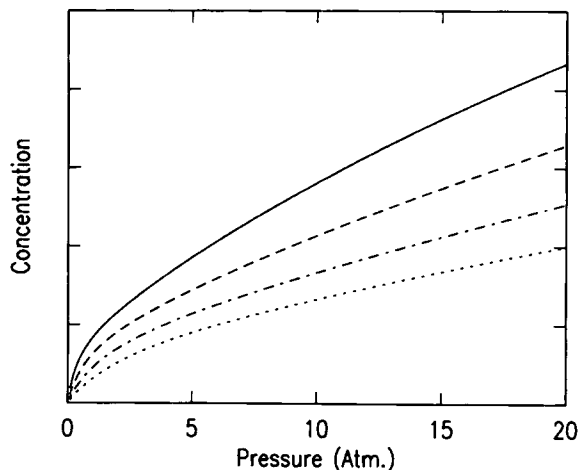
Table I   Temperature Dependences of the Various Dual-Sorption Parameters

	k_D	b	$C_{H'}$
30	3.11	0.873	27.4
40	2.28	0.817	22.1
50	1.64	0.582	19.9
60	1.18	0.370	18.9

tribution to the observed temperature dependence of a family of sorption isotherms. The results of Figure 3 parallel the sorption data of Sada et al. (Fig. 1 of Ref. 1) closely.

One can fit the "data" of Figure 3 to a dual-sorption model to obtain the temperature dependences of the various dual-sorption parameters. These are given in Table I. The temperature dependence of the Langmuir capacity constant has been plotted in Figure 4, which shows that the Langmuir capacity constant obtained from this fit to a dual-sorption expression decreases by roughly 50% of its value over a range of 30°C. One, therefore, concludes that the temperature dependence of the Langmuir capacity constant obtained from a dual-sorption analysis of data will reflect not only polymeric structural changes, but differences in the redistribution of the molecules among the available binding sites in the polymer.

Finally, it should be emphasized that the three-state model has been chosen for illustrative purposes. We have not attempted a detailed fit of the experimental CO_2 polyimide sorption data.[1] It is expected that a somewhat different density-of-states distribution would yield a closer correspondence with the experimentally observed temperature dependences of the reported dual-mode sorption parameters.[1] This suggests that significant variation

Figure 3   Sorption isotherms at four temperatures for the "three-state" model: (———) 30°C; (– – –) 40°C; (– · –) 50°C; (· · ·) 60°C.
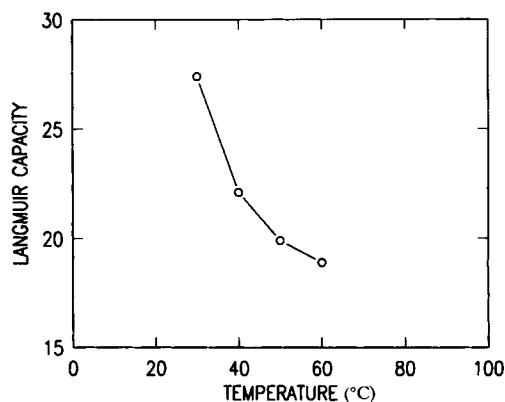
Figure 4   Langmuir capacity constant as a function of temperature (°C).

of the polymeric structure at temperatures well below the glass transition temperature may not be required to rationalize the shapes and temperature dependences of a family of polyimide sorption isotherms.

CONCLUSIONS

The present paper has attempted to demonstrate the limited utility of a "dual-sorption theory" in providing microscopic structural information concerning the polyimides. In particular, it has been demonstrated that the presence of temperature-dependent structural changes at temperatures well below the glass/crystalline phase transition cannot be unambiguously inferred from an examination of the temperature dependence of the Langmuir capacity constant. We have derived an expression for the sorption isotherm assuming that the polymer provides a distribution of different binding sites for the gas molecules. In connection with sorption, as well as with other phenomena, one should expect not only "extrinsic" variations with temperature that reflect structural changes, but "intrinsic" changes as well, which reflect the redistribution, at fixed structure, of gas molecules among different polymeric binding sites. Furthermore, for a narrow range of temperatures, well below the structural phase transition, one might expect the "intrinsic" changes to predominate. One further surmises that understanding details of gas sorption at the microscopic level of such materials will be an exceedingly complex task. The polyimides, for example, do not undergo a singular glass transition. Wide-angle X-ray diffraction studies[30] indicate the presence of regions with a molecular structure that is characteristic of smectic order. Other experiments have suggested the presence of amorphous regions. It is apparent that different sets of experiments probing different microscopic details of molecular binding and migration in the polyimides will be required before a detailed microscopic picture of the gas sorption and permeability in these materials emerges.

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