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Sorption of small molecules in polymeric media

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HIGHLIGHTS

- Gas sorption isotherms in polymeric media via Lambert function.
- Universality of the Lambert function.
- Two parametric fits not inferior to the three parametric ones of the dual mode.

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ABSTRACT

We discuss the sorption of penetrant molecules from the gas phase by a polymeric medium within a model which is very close in spirit to the dual sorption mode model: the penetrant molecules are partly dissolved within the polymeric matrix, partly fill the preexisting voids. The only difference with the initial dual sorption mode situation is the assumption that the two populations of molecules are in equilibrium with each other. Applying basic thermodynamics principles we obtain the dependence of the penetrant concentration on the pressure in the gas phase and find that this is expressed via the Lambert W-function, a different functional form than the one proposed by dual sorption mode model. The Lambert-like isotherms appear universally at low and moderate pressures and originate from the assumption that the internal energy in a polymer–penetrant–void ternary mixture is (in the lowest order) a bilinear form in the concentrations of the three components. Fitting the existing data shows that in the domain of parameters where the dual sorption mode model is typically applied, the Lambert function, which describes the same behavior as the one proposed by the gas–polymer matrix model, fits the data equally well.

1. Introduction

The mechanisms of gas sorption in polymeric media have provided an interesting challenge to scientists of different areas in the last decades. This interest was not merely theoretical. The importance acquired by polymeric materials in industry made a good description and deep understanding of this phenomenon necessary. The description and interpretation of experimental data follows within empirical models which combine some simple functions in which the experimental data may be fitted with a physical explanation of the corresponding choice. Many sorption laws have been proposed and successfully used.

The oldest and simplest one, the Henry's law, states that the amount of molecules sorbed by the medium is linearly proportional to the gas pressure:

$$C = k_D P \tag{1}$$

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Nomenclature

EC	Ethyl Cellulose
PEMA	Poly(Ethyl Methacrylate)
PETP	Poly(Ethylene Terephthalate)
PMMA	Poly(Methyl Methacrylate)
PS	Polystyrenes
PVA	Poly(Vinyl Acetate)
PVC	Poly(Vinyl Chloride)
PVCH	Poly(Vinyl Cyclohexane Carboxylate)

where C is the gas concentration in the polymeric medium, P the gas pressure outside of the polymer and k_D the solubility coefficient. This kind of behavior can be observed in the ideal gas case at low pressures, or for higher pressures in rubbery polymers. More generally, Henry's law holds when the interaction between penetrant molecules and polymer ones is negligible compared to the polymer–polymer one. In all other cases deviations from the Henry's law are observed.

In 1953 Barrer et al. introduced the dual mode of sorption model for glassy polymers [1]. In this model the penetrants are divided into two different populations in which the first one obeys the Henry's law, while the second one, being captured in frozen pores, follows a different, Langmuir mode. This Langmuir mode is switched on as soon as the system is cooled below its glass transition temperature. The total sorption law is given by the sum of these two modes,

$$C = k_D P + \frac{C_H bP}{1+bP}, \tag{2}$$

where C_H is the Langmuir's sorption capacity parameter and b is the affinity parameter. The model is probably of the widest use among all models of sorption isotherms, and its extensive discussion is given in Ref. [2].

More recently, Sefcik and Raucher introduced the Gas–Polymer Matrix Model [3] in which the relation between concentration and pressure is given by the transcendental equation

$$C = S_0 e^{-\alpha^* C} P \tag{3}$$

where α^* is a constant and S_0 the solubility coefficient at zero concentration. This model does not imply the existence of two different populations of solute molecules but assumes an interaction between particles and medium. This interaction modifies the structure of the polymer matrix leading to enhancing of the motion of molecules through it. The solution of Eq. (3) is given by

$$C = \frac{1}{\alpha^*} W\left(\alpha^* S_0 P\right) \tag{4}$$

where $W(z)$ is the Lambert function, the solution of the transcendental equation $We^W = z$.

Above the glass transition temperature, sorption isotherms also deviate from the Henry straight line when the pressure is increased. This behavior has been successfully reproduced by the Flory–Huggins [4] mode of sorption given by

$$\phi_1 \cdot \exp\left[(1-\phi_1) + \chi(1-\phi_1)^2\right] = a \tag{5}$$

where ϕ_1 is the penetrant volume fraction (connected with C), χ is the Flory–Huggins parameter and a is the penetrant activity in the gas phase, connected with the gas pressure. This mode is valid for binary mixtures when the interaction between sorbed molecules is the most relevant one. The sign of χ characterizes the shape of the corresponding sorption isotherm: when this is negative, the penetrant is a good solvent for the polymer and the $C(P)$ dependence is convex. In the bad solubility case $\chi > 0$ the corresponding sorption isotherm is concave.

Many variations and combinations of these models have been also proposed, see Refs. [5–10] just to name a few. In these models, sorption isotherms show corrections to the principal models discussed above, or appear in form of superpositions of a Matrix Model and Langmuir dependencies, or of two different Langmuir dependencies, etc.

We note that common for most of the models of the absorption in glassy polymers is the assumption of the preexisting free volume, i.e. "holes" frozen due to quenching into the glassy state. This is also an explicit assumption done in the dual sorption mode model. The model however does not take into account that populations of sorbent molecules dissolving the polymer and absorbed in holes do essentially coexist in the same piece of a polymeric medium. In the present work we show that a consequent implementation of the "dual-mode" sorption model (including parallel mechanisms of filling of the preexisting holes in the polymeric matrix by the penetrant molecules and the dissolution of the matrix in the penetrant) leads at small pressures to a universal form of the sorption isotherm, namely to the one described by the Lambert function. No additional assumptions done in formulation of the phenomenological Gas–Polymer Matrix Model are necessary to obtain the result.