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Modeling of vapor sorption in glassy polymers using a new dual mode sorption model based on multilayer sorption theory

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Abstract

Conventional dual mode sorption (CDMS) model is one of the most effective models in describing vapor sorption isotherms with a concave towards the activity axis in glassy polymers, while engaged species induced clustering (ENSIC) model has been approved to be highly successful in modeling vapor sorption isotherms in polymers with a convex to the activity axis (BET type III) over a wide range. However, neither of them is effective to describe other types of vapor sorption isotherms, especially sigmoidal isotherms. The Guggenheim–Anderson–de Boer (GAB) model fits extremely well with sigmoidal isotherms such as some vapor especially water vapor sorption data in food and related natural materials. However, one assumption of the GAB model for vapor sorption in glassy polymers is inconsistent with the fact that there are two species of sorption sites as the CDMS model assumes. Based on multilayer sorption theory on which the Guggenheim–Anderson–de Boer (GAB) model is based, a new dual mode sorption (DMS) model for vapor sorption in the glassy polymers is deduced. The mathematical meanings and the physicochemical significances of the parameters in the new model are analyzed. The new model has been verified experimentally by some special cases. Comparisons of the new DMS model with the CDMS and the ENSIC models prove that only the new model fits extremely well with all types of vapor sorption isotherms in the glassy polymers.

Keywords: Glassy polymer; Vapor sorption; GAB model

1. Introduction

There are three main types of vapor sorption isotherms in glassy polymers, as shown in Fig. 1(a)–(c), where c and a are, respectively, penetrant concentration and activity in the polymers.

Type 1 is concave to activity axis at low activities and almost linear at higher activities [1–3], as shown in Fig. 1(a). Most of the vapor sorption isotherms in glassy polymers are Type 1, such as water vapor sorption isotherms in two polyimide copolymers, PMDA–50DDS/50ODA and BPDA–50DDS/50ODA at 30 °C [2], as illustrated in Fig. 13.

Type 2 regularly referred to as BET type II, is a sigmoidal isotherm, which is concave to the abscissa at low activities and convex at high activities [4–10], as illustrated in Fig. 1(b). There is an inflection point in the isotherm. Many vapor sorption isotherms in glassy polymers are this type, such as methanol vapor sorption in cellulose acetate [10], as shown in Fig. 16.

Type 3 is always convex to the activity axis [6,10], as shown in Fig. 1(c). Only a few of vapor sorption isotherms in glassy polymers belong to this type, such as ethanol vapor sorption in cellulose acetate [10], as illustrated in Fig. 18.

Two special isotherms, Type 4 and Type 5, both of which are Type 3 actually, should be specially mentioned. Type 4 looks like Type 1, because the downward curvature at relatively high activities is too inconspicuous to be discerned, such as water and ethanol vapor sorption in poly(vinylchloride) (PVC) at 40 °C [11], as shown in Fig. 14. Type 5 looks like Type 3, because the upward curvature at low activities is too inconspicuous to be discerned, such as water vapor sorption in cellulose acetate at 25 °C [10], as displayed in Fig. 17.

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List of symbols

a	penetrant activity in a polymer
A	temperature-dependent constant in GAB model
A_0	pre-exponential factor of a temperature-dependent constant in GAB model
A'	temperature-dependent constant in new DMS model
b	microvoid affinity constant based on pressure
b_0	microvoid affinity constant based on activity
c	penetrant concentration in a glassy polymer
c_1	penetrant concentration in matrix region of a glassy polymer by new DMS model
c_2	penetrant concentration in microvoids of a glassy polymer by new DMS model
c_{D}	penetrant concentration in matrix region of a glassy polymer by CDMS model
c_{H}	penetrant concentration in microvoids of a glassy polymer by CDMS model
C'_{H}	Langmuir saturation constant
C_{p}	monolayer sorption capacity
C_{p1}	monolayer sorption capacity in matrix region of a polymer
C_{p2}	monolayer sorption capacity in microvoid region of a polymer
C'_{p}	weighted mean value of sorption capacity of a polymer to sorbate molecules
$\overline{C}_{\mathrm{p}}$	weighted mean value of polymer sorption capacity to sorbate molecules based on $\bar{s}_1$ and $\bar{s}_2$
H	heat given off when a molecule enters sorbed sites of a polymer
H_{L}	heat of condensation of a pure vapor
H_{m}	heat of sorption of monolayer of a vapor
H_{n}	heat of sorption of multimolecular layers of a vapor
k	temperature-dependent constant in GAB model
k'	temperature-dependent constant in new DMS model
k_0	pre-exponential factor of a temperature-dependent constant in GAB model
k_{D}	Henry's law dissolution constant based on pressure
k_{D0}	Henry's law dissolution constant based on activity
k_{p}	affinity of a penetrant molecule towards a polymer site
k_{s}	affinity of a penetrant molecule towards a like molecule
n	n-layer sorption
n_{p}	polymer segment number
n_{s}	sorbed solvent molecule number
p	pressure
p_0	vapor saturation pressure
R	gas constant
R^2	square of the correlation between the response values and the predicted response values
s	average number of molecules per sorbed site
s_1	average number of molecules per sorbed site in matrix region of a polymer
s_2	average number of molecules per sorbed site in microvoid region of a polymer
$\bar{s}_1$	average values of average number of sorbed molecules per site in matrix region of a polymer over the entire range of activity
$\bar{s}_2$	average values of average number of sorbed molecules per site in microvoids of a polymer over the entire range of activity
T	temperature
T_{g}	glass transition temperature
y_i	experiment value
$\hat{y}_i$	predicted value
$\bar{y}_i$	mean value

List of abbreviations

AP	pyromellitic anhydride
BET	Brunauer, Emmet and Teller
BPDA	biphenyl tetracarboxylic dianhydride
CDMS	conventional dual mode sorption
DMS	dual mode sorption
ENSIC	Engaged species induced clustering
GAB	Guggenheim–Anderson–de Boer
MDI	macrodiisocyanate
NTDA–*o*BAPBDS	a copolymer by copolymerization of 1,4,5,8-naphthalenetetracarboxylic dianhydride (NTDA) and 2,2′-bis(4-aminophenoxy)biphenyl-5,5′-disulfonic acid (*o*BAPBDS)
NTDA–BAPBDS	a copolymer by copolymerization of 1,4,5,8-naphthalenetetracarboxylic dianhydride (NTDA) and 4,4′-bis(4-aminophenoxy)biphenyl-3,3′-disulfonic acid
NTDA–*o*BAPBDS/*m*BAPPS(2/1)	a copolymer by copolymerization of 1,4,5,8-naphthalenetetracarboxylic dianhydride (NTDA) and 2,2′-bis(4-aminophenoxy)biphenyl-5,5′-disulfonic acid (*o*BAPBDS)/bis [4-(3-aminophenoxy)-phenyl] sulfone (mBAPPS)
ODA	oxydianiline
PCL	poly(caprolactonediol)
PDMS	poly(dimethylsiloxane)
PET	poly(ethylene terephthalate)
PMDA	pyromellitic dianhydride
PPG	poly(propyleneglycol)
PPO	poly(propylene oxide)
PTMG	poly(tetramethyleneglycol)
PUI	poly(urethaneimide)
PVC	poly(vinylchloride)
SSE	sum of squares due to error
SSR	sum of squares of regression
SST	total sum of squares
TFE/BDD65	a glassy copolymer containing 65 mol% 2,2-bis (trifluoromethyl)-4,5-difluoro-1,3-dioxole (BDD) and 35 mol% tetrafluoroethylene
TFE/BDD87	a glassy copolymer containing 87 mol% 2,2-bis (trifluoromethyl)-4,5-difluoro-1,3-dioxole (BDD)