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Simple and complex sorption–solution isotherms for membrane polymers: A statistical thermodynamic fluctuation theory

Seishi Shimizu^{a,*}, Ondřej Vopička^b, Karel Friess^b, Nobuyuki Matubayasi^c

^a York Structural Biology Laboratory, Department of Chemistry, University of York, Heslington, York YO10 5DD, United Kingdom

^b Department of Physical Chemistry, University of Chemistry and Technology, Prague, Technická 5, 166 28 Prague, Czech Republic

^c Division of Chemical Engineering, Graduate School of Engineering Science, Osaka University, Toyonaka, Osaka 560-8531, Japan

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ABSTRACT

Simple, site-specific adsorption isotherm models, such as GAB and other generalizations of BET, fit strikingly well to experimental isotherms of simple shapes for glassy and rubbery polymers. However, the structures of dense polymers do not necessarily resemble the unrestricted layer-by-layer adsorption mechanism on one type of sorption site assumed by these models. Since polymers contain micropores, sorptive likely (ad)sorbs on the internal surfaces of the free (accessible) volume voids, and dissolves in the polymer phase. While the empirical dual mode sorption model and its variants address this duality, other common models assume chiefly only one of the two mechanisms. Moreover, the simplified models do not fit complex isotherms, such as those for alcohols and poly[(trimethylsilyl)propyne] (PTMSP). The statistical thermodynamic fluctuation theory is adopted here to capture the sorption-solution duality consistently even for the complex isotherms. The statistical thermodynamic ABC isotherm derived from this theory involves the sorbate-sorbent and mono-, di-, and tri-sorbate interactions expressed by sorbate number correlations. This work shows that BET, GAB, dual-mode sorption model, Flory-Huggins, and ENSIC models are special cases of the ABC isotherm. The isotherm multiplicativity principle has been derived from the number fluctuation relationship to model complex isotherms.

1. Introduction

In theory, the functional shape of a sorption isotherm should reflect its underlying molecular interactions [1–5]. In practice, however, several out of the 100+ known isotherm models [6,7], each with a different mechanistic assumption [8], can fit an experimental isotherm comparatively well [8,9]. Moreover, some of the most popular models, such as the dual mode sorption (DMS) model, BET, and GAB, are semi-empirical or have been applied beyond their original assumptions (i.e., site-specific, unrestricted layer-by-layer adsorption mechanism on a uniform surface) [8,10,11].

To bridge the gap between theory and practice, which inspired pessimism for isotherm analysis [8], the statistical thermodynamic fluctuation theory [12] whose tradition goes back to Kirkwood-Buff solution theory [13] and its inversion [14] can be used. The sorbate-sorbate interactions can be evaluated *in a model-independent manner* from the gradient of an isotherm [12,15–17]. Moreover, two simple statistical thermodynamic isotherms, the ABC isotherm (representing mono-, di-, and tri-sorbate interactions at the interface, Fig. 1(a)) [15,16] and the cooperative isotherm (capturing the *m*-sorbate cooperative sorption, Fig. 1(b)) [18,19], can, in

* Corresponding author.

E-mail address: seishi.shimizu@york.ac.uk (S. Shimizu).

combination, fit all six IUPAC solid/vapor isotherm types [20] with a clear physical meaning of all their parameters [15,16,18,19]. The physically sound sorption model is clearly a prerequisite for modeling transport in dense materials using the solution-diffusion mechanism [21].

Armed with the above recent achievements, this paper focuses on a challenging topic of vapor and gas sorption on glassy and rubbery polymers as an essential step towards elucidating gas separation and purification through polymer membranes [22–24]. The isotherms for single-component sorption in polymers are already more complex than simple adsorption as they result from multiple simultaneous processes: adsorption on surfaces, filling of micropores (free volume voids), dissolution into the bulk polymer, and its swelling [20,25–28]. Therefore, the aim of this paper is twofold:

- I. to establish a universal isotherm theory that encompasses surface adsorption, formation of aggregates of sorbate molecules, and (dis)solution into sorbent interior that can incorporate sorbent structure changes; and
- II. to clarify and demonstrate how simple isotherm equations can be combined to model sorption isotherms with more complex functional shapes.

In the following, we will articulate why our twofold aim is crucial.

Need for an Adsorption-Solution Isotherm Theory. The vapor (gas) isotherms on glassy polymers exhibit a dual character of sorption and solution; vapor (gas) molecules not only adsorb onto but also dissolve into polymers [29–31]. For the glassy polymers of high free volume, swelling dominated by the filling of the adsorption centers was observed at low sorptive saturations [32–35]. It thus seems erroneous to neglect the adsorptive contribution. This has been recognized since the DMS model [36–42], which considered an isotherm as the sum of the “ordinary dissolution” and “hole-filling” processes, for which Henry’s law or Flory-Huggins term and Langmuir’s case I adsorption model were used and which captures a substantial part of Type II isotherms (Fig. 1(a)) [20,37,42,43]. However, this brings persistent questioning of how “immobilized” the adsorption process is [40–42,44,45] as the difference in mobility between the two processes has not been clarified. The duality of (ad)sorption-(dis)solution, in the language of the DMS model, has led to the two current strategies for modeling [27] assuming only one key mechanism and providing acceptable results for numerous systems. (a) Applying the BET and GAB adsorption isotherm models and their modifications [25,46], which are correlative and neglect dissolution. (b) The calculation of chemical potentials using equations of state via the nonequilibrium theory of glassy polymers [26–30], which are partially predictive (contain adjustable constants) and neglect adsorption. The duality of approaches (see Ref [27] for comparing some of these models) invokes the principal question of how gas and vapor isotherms on polymers can be modeled by combining dissolution and adsorption. The aim here is to develop a theoretically founded isotherm equation with the quality of quantitatively correlating not only the simple isotherm types, for which the both above strategies usually perform well, but also the complex ones for which these strategies do not perform well, such as those for the sorption of alcohols in poly[(trimethylsilyl)propyne] (PTMSP) [32].

In contrast to the sorption in glassy polymers, sorption isotherms for rubbery polymers and polymer solutions routinely show shapes following the lattice models [47–49] of dissolution without apparent hole-filling contribution. It was also reported that a glassy polymer undergoes solvent-induced glass transition at a particular sorbate loading and then follows the shape of an isotherm common

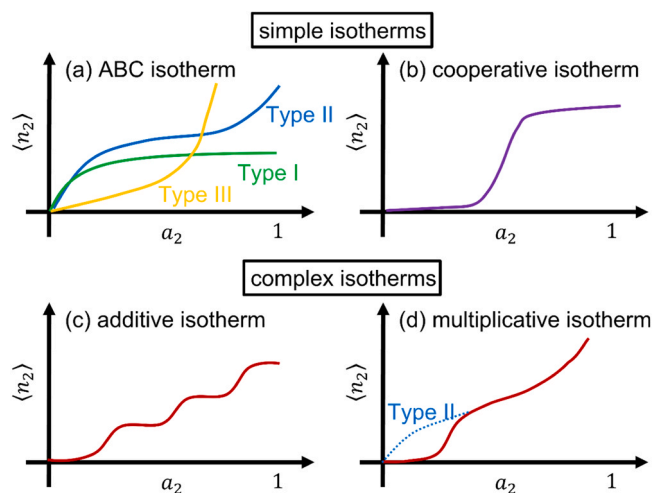


Fig. 1. Schematic representation of simple (a and b) and complex (c and d) isotherms. (a) The ABC isotherm (Eq. (5a)) for IUPAC Type I ($A > 0$, $B < 0$, $C = 0$), Type II ($A > 0$, $B < 0$, $C > 0$), and Type III ($A > 0$, $B > 0$, $C \geq 0$) isotherms [51]. (b) The cooperative isotherm for IUPAC Type V isotherms. (c) The additive isotherm, similar in shape to the IUPAC Type VI [20], observed for heterogeneous porous materials. Type IV also belongs to this category. (d) The multiplicative isotherm (solid red curve), observed for glassy polymers and powders; the behavior of IUPAC Type II at low a_2 is shown for comparison (dotted blue curve). Both classes can be modeled by combining several isotherm equations. The theory for modeling (c) is founded on the statistical independence of microscopic-sized patches and can be implemented as the sum of several cooperative isotherms [18,19]. The theory for (d) will be developed in this paper. How to distinguish (c) and (d) will also be discussed.

for the rubbers [50]. Generally, “holes” decay as the thermal motions of the chains are less hindered in the plasticized polymer, and “dissolution” prevails. Although this interpretation is meaningful, its conversion to a model equation is not straightforward.

Modeling Complex Isotherms. Simple isotherm equations (Fig. 1(a) and (b)) alone are insufficient for capturing complex isotherm shapes. The first class of complex isotherms is the multiple-stepwise isotherms (Fig. 1(c)), observed for porous materials of heterogenous nature (and may be considered the *extension* of Type VI [20], which was defined initially as “representative of layer-by-layer adsorption on a highly uniform nonporous surface” [20]). This class of isotherms can be modeled as the *addition* of cooperative isotherms (Fig. 1(d)) [19] when the interface is composed of statistically independent microscopic (nano-sized) patches, such as pores and crevices [19]. Such isotherm additivity is founded on the thermodynamics of small systems [52,53] and its statistical thermodynamic generalization [18,19,54]. In the context of sorption into glassy polymers, isotherm additivity has been known empirically and implemented in the dual-model [1,36,39,40].

However, additivity is not the exclusive origin of complex isotherms. The second class of complex isotherms (shown schematically in Fig. 1(d)) was discovered for alcohol vapor sorption in PTMSP, a glassy polymer of high free volume [31,32,55,56], which is different in shape from the additive isotherms (Fig. 1(c)). Isotherms with a similar functional shape have also been reported for graphitized carbon blacks [57,58].

Isotherm additivity has failed to capture this class (or anomaly), which was demonstrated by the need for an artificial threshold activity value above which an exponential isotherm term switches on suddenly [32,56]. Other empirical models were applied to this task, such as that by Fowler [32,59] and the model assuming the pore filling and formation of associates [60]. Alternatively, a successful fitting was achieved by modifying the GAB isotherm model, making one of the GAB constants vary exponentially with sorptive (and sorbate) activity to capture the initial cooperative rise [55]. The approach utilizing the calculation of chemical potentials from equations of state also shows discernible deviations from the experimental isotherms despite containing adjustable parameters (Fig. 8 in [26], Fig. 5 in [30]).

The need for empirical models and the shortcomings of the models based on the chemical potential calculation point to the need for a rational strategy for combining several isotherm contributions systematically.

Our Strategy. The first step is establishing a theory of isotherms that can be applied to sorption and solution. This can be achieved by taking advantage of the mathematical analogy between adsorption and solution that will be established in Section 2. With the sorption-solution analogy, the ABC [15,16,51] (Fig. 1(a)) and cooperative [18,19] (Fig. 1(b)) isotherms (see the second paragraph of the Introduction) will apply to glassy and rubbery polymer membranes with their dual sorption-solution character of isotherms. With this new advantage, the second step is to establish how complex isotherms can be constructed by combining simple vapor sorption isotherms, amongst which the “additive isotherms” (Fig. 1(c)) constitute a subcategory. Here, “multiplicative isotherms” (Fig. 1(d)) will be introduced as a new subcategory of complex isotherms. We will derive the multiplicative rule under the condition that the sorbate excess numbers, the measure of sorbate-sorbate interaction, can be expressed as a sum of several different contributions (Section 2). We will demonstrate that (i) the statistical ABC isotherm handles the sorption-solution dualism effortlessly, can be applied to Types II and III isotherms alike, and unifies the previous fittings using different models (such as DMS, Flory-Huggins, and ENSIC models), giving them universal statistical thermodynamic interpretation, and that (ii) the anomalous alcohol vapor adsorption on glassy polymers can be modeled by isotherm multiplicativity, thereby clarifying the underlying sorption mechanism (Section 3). We will also prove that the additive and multiplicative isotherms are indeed different subcategories of composite isotherms (Section 3).

2. Theory

2.1. Fluctuation sorption theory

2.1.1. Notation

Here, we briefly summarize the fundamentals of the fluctuation sorption theory [12,15,16]. Let species 1 and 2 be sorbent (polymer) and sorptive/penetrant, respectively. A sorption isotherm describes the dependence of $\langle n_2 \rangle$ (i.e., the ensemble average of the number of the sorbate, n_2) on the activity of sorbate a_2 that equals, once the phase equilibrium is attained, the relative pressure of the sorptive in the gas phase [12,15,16]. As explained in the following paragraphs, the fluctuation sorption theory quantifies sorbate-surface and sorbate-sorbate interactions from an isotherm and its gradient.

2.1.2. Unifying adsorption and solution

Our first aim was to establish a universal isotherm theory encompassing (a) (dis)solution into sorbent interior that can incorporate sorbent structure changes and (b) surface adsorption (see Section 1). This can be achieved by the mathematical analogy between (a) sorbate-sorbent phase equilibrium with no sorbent evaporation and (b) the generalized Gibbs adsorption isotherm (see Supporting Information A) [15,51]. The fundamental relationship for (a) links how the chemical potential of sorbent (μ_1) depends on that of sorbate (μ_2) to the sorbate excess number per unit sorbent quantity, $\langle n_2 \rangle$, via

$$-\left(\frac{\partial \mu_1}{\partial \mu_2}\right)_{T, N_1^g=0} = \langle n_2 \rangle \quad (1a)$$

where $\langle n_2 \rangle$ is defined as the sorbate surface excess (i.e., the difference in the quantities of sorbate in the system $\langle N_2^s \rangle$ and in the gas reference system $\langle N_2^g \rangle$) per the quantity of sorbent in the system $\langle N_1^s \rangle$ as

$$\langle n_2 \rangle = \frac{\langle N_2^* \rangle - \langle N_2^g \rangle}{\langle N_1^* \rangle} \simeq \frac{\langle N_2^* \rangle}{\langle N_1^* \rangle} \quad (1b)$$

in which the dilute $\langle N_2^g \rangle$ can be neglected. We emphasize here that the system (*) contains the sorbent interior. This is the crucial difference to adsorption, whose fundamental relationship relates the dependence of interfacial free energy per unit sorbent quantity (F) on μ_2 to the sorbate surface excess, defined as the difference between the quantities of sorbate in the system $\langle N_2^* \rangle$ and in the reference states (sorbent interior $\langle N_2^s \rangle$ and gas (vapor) $\langle N_2^g \rangle$) as

$$-\left(\frac{\partial F}{\partial \mu_2}\right)_T = \langle n_2 \rangle = \frac{\langle N_2^* \rangle - \langle N_2^s \rangle - \langle N_2^g \rangle}{\langle N_1^* \rangle} \simeq \frac{\langle N_2^* \rangle}{\langle N_1^* \rangle} \quad (1c)$$

where, again, the dilute gas (vapor) $\langle N_2^g \rangle$ can be neglected, and under the common assumption that sorptive cannot penetrate the sorbent, $\langle N_2^s \rangle = 0$ [16]. There is no distinction between (a) and (b) from an experimental perspective. This is because both (a) and (b) measure the amount of sorbate per unit sorbent quantity. Consequently, Eq. (1a-c) establish a relationship between $\langle n_2 \rangle$ and the equation of states for sorption and solution isotherms. To summarize, the fluctuation sorption theory can be applied to adsorption and solution alike, and even to the cases when adsorption and solution take place simultaneously. In contrast, previous isotherm models are limited to adsorption and equation of states models are limited to the solution [27]. Note that the chemical potential in Eq. (1a) can be generalized straightforwardly as the pseudo-equilibrium quantities in the nonequilibrium thermodynamics for glassy polymers (NET-GP) approaches [25–28,30].

2.1.3. Sorbate-sorbate interaction

There are two measures of sorbate-sorbate interaction based on statistical thermodynamics. The first is the excess number of sorbates around a probe sorbate [12,15,16], defined as

$$N_{22} = \frac{\langle N_2(N_2 - 1) \rangle - \langle N_2 \rangle^2}{\langle N_2 \rangle} \quad (2a)$$

which can be evaluated from the ln-ln gradient of an isotherm via [12,15,16]

$$\left(\frac{\partial \ln \langle n_2 \rangle}{\partial \ln a_2}\right)_T = N_{22} + 1 \quad (2b)$$

Eq. (2a and b) are valid for sorption and solution isotherms. Note that the probe sorbate is included in $N_{22} + 1$. Consequently, $N_{22} + 1$ is referred to as the excess cluster number of sorbates [15,18,19,51]. Here, we present a form equivalent to Eq. (2b),

$$\left(\frac{\partial \ln \frac{\langle n_2 \rangle}{a_2}}{\partial \ln a_2}\right)_T = N_{22} \quad (2c)$$

which will play a key role in introducing isotherm multiplicativity in the next subsection.

The second measure is the sorbate-sorbate extended Kirkwood-Buff integral (KBI) [12], G_{22} , defined by normalizing N_{22} by the sorbate concentration, $\langle n_2 \rangle/\nu$. Here, a careful discussion is necessary regarding the definition of ν . For adsorption, ν is the volume of the interface [15]. When absorption is involved, ν represents the volume into which sorptive can penetrate [15]. When sorptive can dissolve into sorbent, forming a single phase, ν is the volume of the entire phase. To generalize all these cases, we generalize the definition of ν as the volume accessible to the sorbate. With this generalized definition, G_{22} can be introduced as [12,15,16]

$$\frac{G_{22}}{\nu} = \frac{N_{22}}{\langle n_2 \rangle} \quad (3a)$$

Just like N_{22} , G_{22} can also be linked to the isotherm, which can be achieved by combining Eqs. (2c) and (3a), as [12,15,16,51]

$$\left(\frac{\partial}{\partial a_2} \frac{a_2}{\langle n_2 \rangle}\right)_T = -\frac{N_{22}}{\langle n_2 \rangle} = -\frac{G_{22}}{\nu} \quad (3b)$$

Consequently, Eq. (3b) shows that G_{22}/ν can be evaluated from the gradient of $a_2/\langle n_2 \rangle$. The sorbate-sorbate G_{22} has been introduced as a generalization of the Kirkwood-Buff solution theory to the interface. (The Kirkwood-Buff [13] and McMillan-Mayer [61] are the two exact theories for liquid solutions that are related to each other at the dilute solute limit (superscript o) via $G_{22}^o = -2B_{22}$, where B_{22} is the second osmotic virial coefficient [62].) We have adopted the Kirkwood-Buff route because it allows G_{22} and N_{22} to change with the sorbate activity.

2.1.4. Sorbate-sorbent interaction

The sorbate-sorbent interaction is also quantified in a twofold manner. The first is the sorbate-surface excess number [12,15,16],

from which the second measure, the sorbate-surface Kirkwood-Buff integral, can also be defined as its normalization by the concentration of the reference gas system, c_2^g , by

$$G_{s2} = \frac{\langle n_2 \rangle}{c_2^g} = \frac{1}{c_2^o} \frac{\langle n_2 \rangle}{a_2} \quad (4)$$

where c_2^o denotes the concentration of the saturated vapor introduced via $a_2 = c_2^g/c_2^o$ [12,15,16]. Note that the pressure in adsorption is expressed relative to the saturation pressure. Hence, the sorptive gas density is measured relative to the value at saturation. Consequently, $\langle n_2 \rangle/a_2$ should practically be regarded as KBI expressed in terms of the ‘‘relative density’’, a_2 . Both $\langle n_2 \rangle$ and G_{s2} can be introduced for solution and sorption isotherms alike and will be employed to establish the multiplicative sorption theory.

2.1.5. Simple statistical thermodynamic isotherms

Two important isotherms can be derived straightforwardly from the excess number (Eq. (2b)) and Kirkwood-Buff integral (Eq. (3b)) relationships. The first is the ABC isotherm,

$$\langle n_2 \rangle = \frac{a_2}{A - Ba_2 - \frac{C}{2}a_2^2} \quad (5a)$$

where A , B , and C represent mono-, di-, and tri-sorbate interactions in the presence of the sorbent, which results from expanding G_{22}/v into sorbate power series [15,16]. The second is the cooperative isotherm,

$$\langle n_2 \rangle = N \frac{A_1 a_2 + mA_m a_2^m}{1 + A_1 a_2 + A_m a_2^m} \quad (5b)$$

where A_1 and A_m are related via $-RT \ln A_1$ and $-RT \ln A_m$ to the mono- and m -sorbate sorption-free energy into one of the N microscopic (nano-sized) patches (such as pores). Under $A_1 = 0$, Eq. (5b) can be derived directly from Eq. (2b), in combination with the linearly decreasing $N_{22}+1$ with coverage; A_1 has been introduced to satisfy Henry’s law if $m \neq 1$ [18,19]. We emphasize that sorbate-sorbate interactions in both isotherms take place in the presence of the sorbent [12,15,16]. Despite their simplicity, the basic isotherms (Eqs. 5a and 5b) can cover all six IUPAC isotherm types [51].

2.2. Conditional sorption

2.2.1. Isotherm multiplicativity

For a complex sorption phenomenon, a simple isotherm (Eq. (5a or b)) alone is insufficient; combining isotherms to account for the multiple sorption steps is necessary. Here, we introduce the concept of isotherm multiplicativity top-down directly from the foundation of the fluctuation sorption theory (Eq. (2c)) and will clarify its significance incrementally throughout this paper. Suppose that the excess number of sorbates around a probe molecule, N_{22} , is expressed as the sum of two contributions, N_{22}^I and N_{22}^II , as

$$N_{22} = N_{22}^I + N_{22}^II \quad (6a)$$

Under this condition, we use Eq. (2c) for N_{22} , as well as for N_{22}^I and N_{22}^II . The additivity of N_{22} leads to the multiplicativity of $\langle n_2 \rangle/a_2$, as

$$\frac{\langle n_2 \rangle}{a_2} = \frac{\langle n_2^I \rangle}{a_2} \frac{\langle \widetilde{n_2}^{II} \rangle}{a_2} \quad (6b)$$

A comparison with Eq. (2c) shows that the multiplicative rule for $\langle n_2 \rangle/a_2$ is essential for the sorbate-surface KBI in the activity units. The intensive nature of $\langle \widetilde{n_2}^{II} \rangle$ is the logical consequence of $\langle n_2^I \rangle$ and $\langle n_2 \rangle$ being in the same unit, i.e., the amount of sorption per unit sorbent quantity. We have shown previously that $\langle n_2^I \rangle$ can be expressed as a sum of contributions from the statistically independent patches (that can be macroscopic or microscopic). Consequently, $\langle \widetilde{n_2}^{II} \rangle$, being a conditional process following $\langle n_2^I \rangle$, is an isotherm per patch, hence an intensive quantity. Following the terminology of conditional probability, we shall call $\langle n_2^I \rangle$ the (unconditional) isotherm of process I and $\langle \widetilde{n_2}^{II} \rangle$ the *conditional* isotherm of process II subject to the process I . In this context, $\langle n_2 \rangle/a_2$ represents a *composite* isotherm in which the processes I and II occur together. Intuitively speaking, the sorbates sorbed in process I act as new sorption sites for process II , as will be clarified in Section 3.

2.2.2. Conditional isotherm equation

Here, we show that the ABC isotherm (Eq. (5a)) can also be used for the conditional isotherm, $\langle \widetilde{n_2}^{II} \rangle$. To do so, our starting relationship is

$$\left(\frac{\partial \ln \langle \widetilde{n}_2^I \rangle}{\partial \ln a_2} \right)_T = N_{22}^I \tag{7a}$$

which can be rewritten as

$$\left(\frac{\partial}{\partial a_2} \frac{a_2}{\langle \widetilde{n}_2^I \rangle} \right)_T = - \frac{N_{22}^I}{\langle \widetilde{n}_2^I \rangle} \tag{7b}$$

Because of the analogy between Eq. (3b) (from which the ABC isotherm, Eq. (5a), has been derived) and Eq. (7b), the ABC isotherm equation for $\langle \widetilde{n}_2^I \rangle$ can be derived by repeating the same argument (Supporting Information B [15,16,51], leading to

$$\langle \widetilde{n}_2^I \rangle = \frac{a_2}{A - Ba_2 - \frac{C}{2}a_2^2} \tag{8a}$$

where A , B , and C represent the mono-, di-, and tri-sorbate interactions in the presence of the sorbent [15,16,51]. However, unlike the ABC isotherm for conventional (i.e., unconditional) isotherms, $\langle \widetilde{n}_2^I \rangle$ is an intensive quantity, being a conditional isotherm acting on a statistically independent patch that constitutes $\langle n_2^I \rangle$. Consequently, we can use normalized Eq. (8a) by A^{-1} and designate A^{-1} as a part of the unconditional process I . As will be demonstrated in Section 3, the following form (the normalized Eq. (8a) with $C = 0$) suffices for practical use as the conditional isotherm:

$$\langle \widetilde{n}_2^I \rangle = \frac{a_2}{1 - K_a a_2} \tag{8b}$$

where $K_a = B/A$. (Normalization is equivalent to removing the A^{-1} contribution and introducing, instead of it, the unconditional process I). When K_a is positive, it can be interpreted as the infinite successive sorbate-sorbate binding constant (see Section 3) [51]. When K_a is negative, $K_p = -K_a$ signifies the interface/vapor partition coefficient [51]. In Section 3, we will demonstrate that Eq. (8b) with a positive K_a is capable of capturing the high a_2 behavior of the composite isotherm illustrated by Fig. 1(d).

2.2.3. Multiplicativity in simple isotherms

Here, we consider the simplest case of sorption multiplicativity that is already present, albeit implicitly, in a simple isotherm for Types I-III. To do so, let us choose a linear isotherm, $\langle n_2^I \rangle = a_2/A$, as the unconditional isotherm (i.e., the ABC isotherm with $B = C = 0$) for step I and Eq. (8b) as the conditional isotherm for step II , $\langle \widetilde{n}_2^I \rangle$. Consequently, the composite isotherm $\langle n_2 \rangle$, in which the processes I and II occur together, can be written down using the multiplicativity rule (Eq. (6b)) as

$$\langle n_2 \rangle = \frac{a_2}{A} \frac{1}{1 - K_a a_2} = \frac{a_2}{A - Ba_2} \tag{9}$$

which is identical in form to the AB isotherm (i.e., the ABC isotherm with $C = 0$). (Repeating the same argument, we can also consider the ABC isotherm as a composite isotherm.) Fig. 2 illustrates how the AB isotherm for Type I and Type II behaviors can be seen as the multiplicative process, in which the conditional process is responsible for sorbate-sorbate interaction in the presence of the sorbent. A favorable sorbate-sorbate interaction ($K_a > 1$) leads to $\langle \widetilde{n}_2^I \rangle > 1$, making the composite isotherm larger than $\langle n_2^I \rangle$. An unfavorable sorbate-sorbate interaction ($K_a < 1$) leads to $\langle \widetilde{n}_2^I \rangle < 1$, making the composite isotherm smaller than $\langle n_2^I \rangle$. Thus, conditional sorption can be considered present even in simple isotherms.

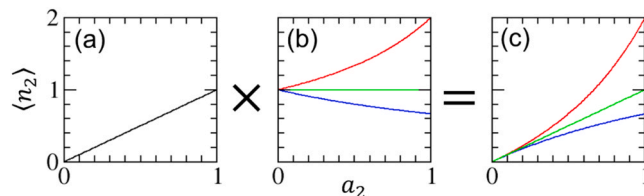


Fig. 2. The simple isotherms of Type I and Type II can be understood as multiplicative isotherms (Eq. (9), with $A = 1$). (a) The linear isotherm ($\langle n_2^I \rangle = a_2$) as the initial process. (b) The conditional process, modeled via the AB isotherm ($\langle \widetilde{n}_2^I \rangle$, Eq. (8b)) with favorable (red, $K_a = 0.5$), unfavorable (blue, $K_a = -0.5$), and zero (green, $K_a = 0$) sorptive-sorptive interactions. (c) The composite isotherm via the multiplicative process from (a) and (b).

2.3. Multiplicative sorption isotherms

2.3.1. Capturing initial cooperativity

Here, we construct a sorption isotherm equation based on the multiplicative rule (Eq. 6b) to reproduce multiplicative composite isotherms illustrated in Fig. 1(d). The departure from a simple ABC isotherm is necessitated to capture the initial cooperativity [55], which can be incorporated by replacing the linear unconditional isotherm in the previous paragraph with the cooperative isotherm,

$$\langle n_2^I \rangle = N \frac{A_1 a_2 + mA_m a_2^m}{1 + A_1 a_2 + A_m a_2^m} \quad (10a)$$

where N is the number of independent patches per unit sorbent quantity, m is the cooperative sorbate cluster size, and $-RT\ln A_1$ and $-RT\ln A_m$ are the free energy of sorbing one and m sorptives, respectively [18,19]. Combining Eq. (10a) with the AB conditional isotherm (Eq. 8b), we obtain the following composite isotherm in which the processes I and II occur together:

$$\langle n_2 \rangle = N \frac{A_1 a_2 + mA_m a_2^m}{1 + A_1 a_2 + A_m a_2^m} \frac{1}{1 - K_a a_2} \quad (10b)$$

Note that other isotherm equations may be chosen for $\langle n_2^I \rangle$ and $\langle \widehat{n_2^{II}} \rangle$.

2.3.2. A graphical interpretation of cooperativity

To facilitate interpretation and sense-check the fitting, the cooperative isotherm (Eq. (10a)) is rewritten in the following manner:

$$\langle n_2^I \rangle = N \frac{A_1 a_2 + m \left(\frac{a_2}{a_m} \right)^m}{1 + A_1 a_2 + \left(\frac{a_2}{a_m} \right)^m} \quad (11a)$$

where $a_m = A_m^{-1/m}$ was introduced, which is advantageous because it corresponds to the point at which the cooperative isotherm rises the steepest when A_1 is negligible (Supporting Information C). Such a point can be located easily and visibly in the experimental isotherm, which is conducive to sense-checking the fitting result. In addition, since $-RT\ln A_m$ signifies the free energy of sorbing m sorptive molecules, $-RT\ln a_m$ signifies the desorption-free energy per sorptive. Note that $-RT\ln a_m$ is identical in form and interpretation to Polanyi's "adsorption potential" [63–65], yet only at $a_2 = a_m$. The cooperative isotherm has other intuitive interpretations: Nm is the saturating capacity and $m/2$ is the steepest gradient at $a_2 = a_m$ (Supporting Information C), both can be examined visually in the isotherm plot (Supporting Information C). Using Eqs. (10b) and (11a), the isotherm can be expressed as

$$\langle n_2 \rangle = N \frac{A_1 a_2 + m \left(\frac{a_2}{a_m} \right)^m}{1 + A_1 a_2 + \left(\frac{a_2}{a_m} \right)^m} \frac{1}{1 - K_a a_2} \quad (11b)$$

Eq. (11b) will be applied to fit experimental data in Section 3. This isotherm (Eq. (11b)) obeys Henry's law at $a_2 \rightarrow 0$, hence we have $\langle n_2 \rangle / a_2 = NA_1$.

3. Results and discussion

3.1. Systematizing isotherm models for polymer membranes

3.1.1. Universal language across isotherm models

Gas and vapor sorption isotherms on polymer membranes exhibit diverse functional shapes, for which isotherm models (such as the DMS [36–41], BET, GAB and their modifications [2–5,55,56,66], ENSIC [67–69], and models based on the lattice models of dissolution [47,70] while the latter two are used mainly to IUPAC Type III isotherms [20] standard for rubbery polymers) have been employed to reproduce their functional shapes. We demonstrate that all these models can be linked to the ABC isotherm. The benefit of adopting the ABC isotherm is threefold:

- applicable to sorption and solution isotherms (aim I in Section 1, see Section 2);
- no interpretive restrictions due to the over-idealized model assumptions; and
- the universal applicability of its parameters signifying mono-, di-, and tri-sorbate interactions.

3.1.2. BET and GAB models

The GAB model [3–5], being an extension of the BET model [2,71], assumes the layer-by-layer adsorption mechanism that has been captured via the monolayer capacity, n_m , the BET constant, C_B (i.e., being related exponentially to the energy of monolayer adsorption [2,71]), and the GAB constant, K_G (which accounts for the difference in binding between the first and outer layers), as

$$\langle n_2 \rangle = \frac{C_B n_m K_G a_2}{(1 - K_G a_2)[1 + (C_B - 1)K_G a_2]} \quad (12a)$$

The GAB model successfully fits vapor sorption in glassy [34,46,55,56,66] and rubbery [72] polymers over wide pressure ranges. However, because of the gap between its multilayer assumptions and the microporous reality of the membrane polymers, the resultant GAB parameters had to be termed as “apparent (equivalent)” [25]. However, such a gap can be eliminated by converting the GAB parameters for polymer/vapor sorption to the ABC isotherm parameters (Eq. 5a, Supporting Information D) via

$$A = \frac{1}{C_B K_G n_m}, \quad B = \frac{2 - C_B}{C_B n_m}, \quad C = \frac{2K_G(C_B - 1)}{C_B n_m} \quad (12b)$$

because the mono-, di- and tri-sorbate interactions are more versatile than the assumptions of the GAB model [15,16,51]. With this conversion, summarized in Table 1, the published GAB parameters (e.g., for PIM-1, PTMSP, or other polymers) can be interpreted via statistical thermodynamics without the overly idealized assumptions of the GAB model. For example, water in Table 1, contradictory to the normal range of the BET parameter, does not pose any problem for the ABC isotherm (see the following paragraph).

From now onwards, we can follow the statistical thermodynamic fluctuation theory to obtain physical interpretation. The negative sign of B (except water) signifies the net sorbate-sorptive repulsion, whereas positive B for water indicates the net water-water attraction. The vapor/interface partition coefficient, K_p , is a model-free quantity that can be evaluated from the parameters of the ABC isotherm via $K_p = -\frac{B}{A}$. Combining this with Eq. (12b), we obtain

$$K_p = (C_B - 2)K_G \simeq C_B K_G \quad (12c)$$

where the approximation is valid for a large C_B . The values of K_p calculated from the GAB model fitting have also been summarized in Table 1. (Note that water, for which $C_B < 2$, yields an unphysical result for K_p .) We have shown in Table 1 that the previous GAB model fitting of the polymer/vapor isotherms [34,55,56,66,72] can be used as a fitting equation to yield the isotherms parameters with a clear physical interpretation (A , B , and C , as well as K_p).

3.1.3. Estimating specific surface areas

The BET surface area has been determined routinely for materials, including glassy polymer membranes (such as PIM-1 [73] and PTMSP [74]). However, applying the BET model to porous materials involving absorption (solution) and micropore filling contradicts their basic assumption of the BET model [16], i.e., unrestricted layer-by-layer adsorption on a uniform surface [10,11,75]. According to IUPAC, the so-calculated areas for porous materials should be considered apparent or effective [20]. Overcoming the involved contradiction requires a reconceptualization of how specific surface area should be evaluated based on the statistical thermodynamic fluctuation theory with broader applicability [16]. The statistical thermodynamic surface area (STSA) is calculated from the sorption capacity at Point M, i.e., the activity at which the sorbate-sorbate exclusion ($-N_{22}$) takes a maximum [75]. The sorption capacity at Point M, $\langle n_2 \rangle_M$, agrees with the BET monolayer capacity for sufficiently large BET constant values (C_B) [16], as has been recommended by the IUPAC [20]. The quality of the estimated surface area can be assessed by the value of $(N_{22})_M$, i.e., the value of N_{22} at Point M. The IUPAC recommendation regarding the BET constant, $80 \leq C_B \leq 150$ [20], translates to $-0.84 \leq N_{22} \leq -0.78$, which is expected to give a good general idea about where N_{22} should approximately be. A larger (more positive) N_{22} indicates the contribution of sorbate-sorbate attraction to sorption, which works against monolayer coverage. A value of N_{22} too close to -1 indicates the micropore filling mechanism instead of the monolayer-multilayer mechanism (by translating the IUPAC recommendation, based on C_B [20], to N_{22}). Thus, STSA has generalized the BET surface area estimation beyond the restrictive BET model assumptions.

Here, we show how STSA can be evaluated based on the GAB model fitting of PIM-1/vapor isotherms (Table 1). Such an approach is

Table 1
ABC isotherm parameters for PIM-1 calculated from the GAB parameters^{a, b}.

	n_m	C_B	K_G	$A \times 10^2$	$B \times 10^1$	$C \times 10^1$	K_p
Methanol	5.45	10.75	0.63	2.71	-1.49	2.10	5.51
Ethanol	4.44	9.23	0.63	3.87	-1.76	2.53	4.55
Propan-1-ol	3.14	20.63	0.63	2.45	-2.88	3.82	11.7
Tetrahydrofuran	3.51	19.85	0.76	1.89	-2.56	4.11	13.6
<i>n</i> -Pentane	2.55	55.59	0.54	1.31	-3.78	4.16	28.9
<i>iso</i> -Pentane	2.02	30.81	0.54	2.98	-4.63	5.17	15.6
<i>n</i> -Hexane	2.26	41.94	0.54	1.95	-4.21	4.66	21.6
1,4-Dioxane	4.16	18.73	0.69	1.86	-2.15	3.14	11.5
Toluene	2.75	22.76	0.7	2.28	-3.32	4.87	14.5
<i>n</i> -Heptane	2.04	45.22	0.56	1.94	-4.69	5.37	24.2
Chloroform	3.59	51.95	0.76	0.706	-2.68	4.15	38.0
Water	1.73	0.99	0.71	82.2	5.90	-0.0829	-0.717
CO ₂	3.43	21.5	2.13	0.637	-2.64	11.8	41.5

^a The GAB parameters (n_m , C_B , and K_G) have been taken from Table 1 of Ref [25]

^b The units of n_m are mmol g⁻¹, and of A , B , and C are g mmol⁻¹. Other parameters are unitless.

beneficial because (i) fitting an isotherm is related to surface area estimation, and (ii) the restrictive assumptions of the GAB model can be eliminated when analyzing porous glassy polymer surfaces. Table 2 summarizes the $\langle n_2 \rangle_M$ and $(N_{22})_M$ calculated (following the relationships derived in Supporting Information E) from the GAB model fitting of PIM-1 [25]. Even though the monolayer capacities from the GAB model are close to $\langle n_2 \rangle_M$, some of the GAB model fitting results yields a high (less negative) $(N_{22})_M$, indicating the contribution of sorbate-sorbate attraction that interferes with monolayer coverage. Moreover, $\langle n_2 \rangle_M$ shows lower dependence on the composition of the actual probing compound (sorbptive).

3.1.4. ENSIC model for Type III sorption

The Type III isotherm behavior observed previously for vapor sorption on Teflon AF 2400 [68,69] and another rubbery polymer, PDMS [76], differs from the GAB model and its assumed monolayer-multilayer mechanism. Consequently, the ENSIC model [67] has been adopted as it describes the Type III isotherms for $k_s > k_p$. This model links the volume fraction of sorbate, ϕ_2 , and sorptive activity, via

$$(k_s - k_p)a_2 = \ln \left[1 + \phi_2 \left(\frac{k_s - k_p}{k_p} \right) \right] \quad (13a)$$

where k_s and k_p are the affinity parameters expressing the interactions between the penetrating sorbate species (k_s) and between the polymer segments and the sorbate molecules (k_p) [69]. These parameters correspond to the ABC isotherm when the latter is expressed in terms of the volume fraction (see Supporting Information D) via

$$A = \frac{1}{k_p} \frac{v_2}{v_1}, \quad B = \frac{k_s + k_p}{2k_p} \frac{v_2}{v_1}, \quad C = \frac{1}{6k_p} \left[4k_p k_s - (k_p + k_s)^2 \right] \frac{v_2}{v_1} \quad (13b)$$

where v_2/v_1 is the sorbate-to-polymer volume ratio originated in the volume fraction used in the lattice model. Thus, the ENSIC and GAB analysis can now be compared within the same theoretical framework of the ABC isotherm. Combining Eq. (13b) with the statistical thermodynamic interpretation of B (see Supporting Information D), we obtain, under $k_s \gg k_p$ (Table 3), the following simplified expressions:

$$\left(\frac{G_{22}}{v} \right)_{a_2 \rightarrow 0} \propto \frac{k_s + k_p}{2k_p} \simeq \frac{k_s}{2k_p} \quad (13c)$$

$$K_a = \frac{B}{A} = \frac{k_s + k_p}{2} \simeq \frac{k_s}{2} \quad (13d)$$

where K_a is the sorbate-sorbate association constant in the presence of the sorbent. Indeed, according to, $k_s \gg k_p$ is satisfied well for methanol ($k_s/k_p \sim 10^3$) and for ethanol, propanol and *iso*-propanol ($k_s/k_p \sim 10^2$), and reasonably for butanol, pentanol, and hexanol ($k_s/k_p \sim 10^1$). A correlation was reported in the previous paper between k_s/k_p and the average cluster size estimated from diffusion [69]. In the framework of the statistical thermodynamic fluctuation theory, k_s/k_p is related to the sorbate-sorbate Kirkwood-Buff integral, which justifies its interpretation as the measure of sorbate-sorbate interaction.

3.1.5. Dual-mode sorption model

Here, we focus on the dual-mode model's assumptions rather than comparing its fitting capabilities with other isotherm models, such as GAB. The DMS model can be expressed as the sum of the "ordinary dissolution process" (the first term, below) and the "hole-

Table 2
Sorbate-sorbate interaction at Point M for PIM-1 calculated from the GAB parameters^{a, b}.

	n_m	C_B	K_G	a_M	$\langle n_2 \rangle_M$	$(N_{22})_M$
Methanol	5.45	10.75	0.63	0.262	4.44	-0.419
Ethanol	4.44	9.23	0.63	0.267	3.48	-0.378
Propan-1-ol	3.14	20.63	0.63	0.226	2.84	-0.570
Tetrahydrofuran	3.51	19.85	0.76	0.190	3.16	-0.563
<i>n</i> -Pentane	2.55	55.59	0.54	0.191	2.46	-0.734
<i>iso</i> -Pentane	2.02	30.81	0.54	0.234	1.89	-0.646
<i>n</i> -Hexane	2.26	41.94	0.54	0.211	2.15	-0.695
1,4-Dioxane	4.16	18.73	0.69	0.212	3.72	-0.550
Toluene	2.75	22.76	0.7	0.198	2.51	-0.590
<i>n</i> -Heptane	2.04	45.22	0.56	0.198	1.95	-0.706
Chloroform	3.59	51.95	0.76	0.139	3.45	-0.725
Water	1.73	0.99	0.71	-	-	-
CO ₂	3.43	21.5	2.13	0.066	3.11	-0.579

^a The GAB parameters (n_m , C_B , and K_G) have been taken from Table 1 of Ref [25].

^b The units of n_m and $\langle n_2 \rangle_M$ are mmol g⁻¹. Other parameters are unitless.

Table 3
ABC isotherm parameters calculated from the ENSIC parameters^a.

	k_s	$k_p \times 10^3$	$\frac{v_1}{v_2} A$	$\frac{v_1}{v_2} B$	$\frac{v_1}{v_2} C$	$\frac{k_s}{2k_p}$
Methanol	4.80	2.78	360	863	-1380	863
Ethanol	3.40	9.13	110	187	-210	186
Propanol	1.82	18.77	53.2	49.0	-28.8	48.5
iso-Propanol	1.66	4.32	231	193	-106	192
Butanol	1.41	20.82	48.0	34.4	-15.5	33.9
Pentanol	1.02	30.78	32.5	17.1	-5.30	16.5
Hexanol	0.70	41.06	24.4	9.02	-1.76	8.52

^a The ENSIC parameters (k_s and k_p) have been taken from Table 3 of Ref [69].

filling process” (the second term) [37,42] via

$$\langle n_2 \rangle = k_H a_2 + \frac{n_m K_L a_2}{1 + K_L a_2} \quad (14a)$$

where k_H is Henry’s Law coefficient of dissolution, n_m is the Langmuir capacity and K_L is the Langmuir constant. First, we derive Eq. (14a) from the statistical thermodynamic fluctuation theory. This can be achieved by postulating sorption as the sum of two statistically independent processes as

$$\langle n_2 \rangle = \frac{a_2}{A_I - B_I a_2 - \frac{C_I}{2} a_2^2} + \frac{a_2}{A_{II} - B_{II} a_2 - \frac{C_{II}}{2} a_2^2} \quad (14b)$$

where we have adopted the ABC isotherms for both processes. We focus on a rather dilute range of a_2 ; assuming that B_I , C_I and C_{II} makes a negligible contribution, we obtain

$$\langle n_2 \rangle = \frac{a_2}{A_I} + \frac{a_2}{A_{II} - B_{II} a_2} \quad (14c)$$

where $k_H = 1/A_I$, $K_L = -B_{II}/A_{II}$, and $n_m = -1/B_{II}$ yields the dual-mode model (Eq. (14a)). Second, we will show that our above rederivation can relax some of the restrictive historic assumptions imposed by adopting the Langmuir model. The Langmuir model assumes that the adsorbed molecules are “immobilized”, which has long been questioned [40–42,44,45]. Our AB isotherm in Eq. (14c), on the other hand, is applicable both for immobilized (site-specific) and non-specific sorption mechanisms; the only underlying physical picture is the sorbate-sorbate repulsion or the negative sorbate-sorbate Kirkwood-Buff integral, which leads to $B_{II} < 0$ [15,16, 51]. Therefore, using the AB isotherm does not mean that immobile adsorption takes place.

We have demonstrated (Tables 1–3) that the statistical thermodynamic ABC isotherm can unify previous isotherm fittings that employed a different isotherm model for each isotherm type and provide a universal interpretation via mono-, di-, and tri-sorbate interactions.

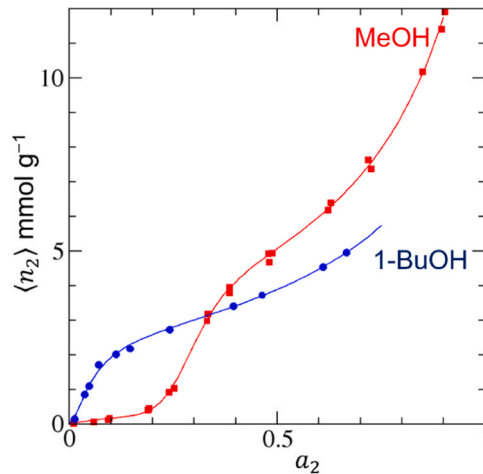


Fig. 3. Experimental sorption isotherms of methanol (at 40 °C, red squares) [56] and 1-butanol (37 °C, blue circles) [31] on poly[(trimethylsilyl) propyne] (PTMSP) versus sorptive activity (a_2), compared to the fitting (solid curves) by the multiplicative sorption isotherm (Eq. (11b)). The fitting parameters are summarized in Table 4.

3.2. Complex sorption via multiplicative isotherms

3.2.1. Alcohol sorption on the inner sites of a glassy polymer membrane

A successful fitting of Eq. (10b) to the experimental methanol and 1-butanol adsorption isotherms on poly[(trimethylsilyl)propyne] (PTMSP) membrane [31,55] is demonstrated in Fig. 3, with the fitting parameters summarized in Table 4. Fig. 4 illustrates the multiplicative nature of this isotherm. The positions of a_m for methanol and 1-butanol (Fig. 3) are approximately at the point of the steepest isotherm gradient, which is consistent with the cooperative isotherm (Eq. (11a)). A larger saturation capacity for methanol reflects its smaller effective size than 1-butanol. K_a for methanol is slightly stronger than for 1-butanol, which may reflect its smaller size and stronger interactions with PTMSP. However, this partitioning coefficient appears very similar for both alcohols, although 1-butanol shows much less pronounced multiplicativity than methanol. Thus, K_a is foreseen to be similar also for other alcohols.

3.2.2. The physical meaning of multiplicative sorption

In Section 2, isotherm *multiplicativity* was introduced top-down based on the *additivity* of sorbate excess numbers. Its significance was attributed to the multiplicative nature of the sorbate-surface Kirkwood-Buff integral. Here, our aim is to clarify the physical meaning of multiplicative sorption. As a first step, starting from Eq. (11b), we will provide an alternative interpretation more in line with the traditional way of thinking yet within the confines of the simple model. As a first step, let us rewrite Eq. (11b) as:

$$\begin{aligned} \langle n_2 \rangle &= N \frac{A_1 a_2 + m \left(\frac{a_2}{a_m} \right)^m}{1 + A_1 a_2 + \left(\frac{a_2}{a_m} \right)^m} \left(1 + \frac{K_a a_2}{1 - K_a a_2} \right) \\ &= N \frac{A_1 a_2 + m \left(\frac{a_2}{a_m} \right)^m}{1 + A_1 a_2 + \left(\frac{a_2}{a_m} \right)^m} + \left[K_a N \frac{A_1 a_2 + m \left(\frac{a_2}{a_m} \right)^m}{1 + A_1 a_2 + \left(\frac{a_2}{a_m} \right)^m} \right] \frac{a_2}{1 - K_a a_2} \end{aligned} \quad (15a)$$

The isotherm (Eq. (15a)) is now expressed as an additive process. The first term is the cooperative isotherm. Let us compare the second term with the AB isotherm (Eq. (9)), focusing primarily on the following correspondence:

$$\frac{1}{A} \leftrightarrow K_a N \frac{A_1 a_2 + m \left(\frac{a_2}{a_m} \right)^m}{1 + A_1 a_2 + \left(\frac{a_2}{a_m} \right)^m} \quad (15b)$$

While in Eq. (9), $1/A$, a constant, is multiplied by the normalized AB isotherm ($a_2/(1 - K_a a_2)$), which signifies the interaction between surface and sorbate, whereas the corresponding factor in Eq. (15b) (i.e., the right-hand side) changes with the sorptive activity. This comparison clarifies the physical picture of multiplicative sorption: the conditional process (II) is sorption to the “interface” consisting not only of the membrane polymer but also of the sorbates cooperatively sorbed via the initial process (I).

A simple reinterpretation of this a_2 dependence (Eq. (15b)) comes from the site-specific binding model despite being limited in scope compared to the generality of statistical thermodynamic theory. This is advantageous for linking isotherm multiplicity to the traditional way of thinking. To this end, the first step is to rederive the AB isotherm using a simple model (detailed in Supporting Information F), an infinite series of binding between sorbates (2), initiated by the first sorbate on the binding site (s), as [77,78]

$$\langle n_2 \rangle = N_s K_s a_2 (1 + K_a a_2 + K_a^2 a_2^2 + \dots) = \frac{N_s K_s a_2}{1 - K_a a_2} \quad (16a)$$

where K_s represents the initial sorbate-sorption site binding constant, with $(n-1)K_a/n$ as the binding constant of n th sorbate molecule (Supporting Information F). The second step is to compare Eq. (16a) to the AB isotherm (Eq. (9)), through which $A^{-1} = N_s K_s$ results as the interpretation of A^{-1} according to the indefinite binding model. Taking this interpretation with Eq. (15a), the multiplicative isotherm (Eq. (15b)) results from the indefinite binding model (Eq. (16a)) if we could modify N_s as

Table 4

Fitting parameters for Eq. (11b) for the sorption isotherms of methanol and 1-butanol on PTMSP^a.

Sorptive	N	m	A_1	a_m	K_a
Methanol	0.395 ^b	7.71	5.73	0.260	0.823
1-Butanol	1.35 ^b	1.84	4.42	0.0576	0.768

^a The experimental data for methanol(at 40 °C) are from Ref [56] and the one for 1-butanol (at 37 °C) are from Ref [31]. ^bThe units are in mmol g⁻¹. Other parameters are unitless.

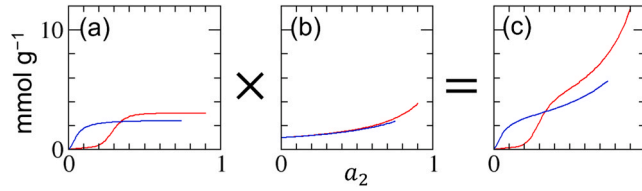


Fig. 4. Understanding the multiplicative processes that comprise the sorption isotherms of methanol [56] (red) and 1-butanol [31] (blue) on PTMSP whose fitting were presented in Fig. 3 and Table 4. (a) The cooperative isotherm, $\langle n_2^1 \rangle$ (Eq. (11a)) as the initial process. (b) The AB isotherm, $\langle \widetilde{n}_2^m \rangle$ (Eq. (8b)) as the conditional process. (c) The composite isotherm, $\langle n_2 \rangle$ (Eq. (11b)), as the multiplicative isotherm comprised of (a) and (b).

$$N_s = \frac{K_a}{K_s} N \frac{A_1 a_2 + m \left(\frac{a_2}{a_m} \right)^m}{1 + A_1 a_2 + \left(\frac{a_2}{a_m} \right)^m} \quad (16b)$$

The increase of sorbate binding sites (N_s), caused by cooperative sorption (the middle of Eq. (16a)), rationalizes the multiplicative sorption isotherm (Eq. (11b)) from a traditional perspective of the indefinite binding model. The sorbates sorbed via the initial cooperative process are acting as new sorbate-“surface” binding sites; the “surface” for the conditional process is the one modified by the sorptive molecules via the initial cooperative process. However, albeit intuitively appealing, such a reinterpretation is limited to site-specific binding and the fortuitous mathematical form of the AB isotherm. (Note that the reinterpretation in terms of the infinite successive binding will become complicated for $C \neq 0$.) Clarifying the precise nature of the initial cooperative sorption (i.e., adsorption or dissolution) requires statistical thermodynamics rather than the binding model, because the latter can capture sorption and solution in the same mathematical framework (Supporting Information A)

3.2.3. Additive versus multiplicative sorption

Can a multiplicative sorption be expressed in terms of additive sorption without introducing constructs such as the increasing sorbate-surface binding site? This question can be answered straightway from the second term of Eq. (15a). Expanding the brackets of its denominator, we obtain

$$\begin{aligned} & (1 - K_a a_2) \left[1 + A_1 a_2 + \left(\frac{a_2}{a_m} \right)^m \right] \\ &= 1 + (A_1 - K_a) a_2 - K_a A_1 a_2^2 + \left(\frac{a_2}{a_m} \right)^m - K_a \frac{a_2^{m+1}}{a_m^m} \end{aligned} \quad (17)$$

When $K_a > 0$, the a_2^{m+1} and a_2^2 terms are negative, and the a_2 term may also be negative when $K_a > A_1$. However, the denominator of cooperative isotherm theory is a partition function that should never contain any negative terms. When $K_a < 0$, all the terms in Eq. (17) become positive. However, the factor in Eq. (15a) becomes negative and makes the second term of Eq. (15a) a negative isotherm, which is against the sorption additivity rule. Thus, we have shown that multiplicative sorption cannot be reduced to additive sorption.

Additive isotherms that exhibit multiple steps (Fig. 1(c)) cannot be expressed by multiplicative isotherms either. To illustrate this point, let us consider the multiplicative sorption consisting of two cooperative isotherms, which can be expressed via the multiplicative rule (Eq. (6b)) as

$$\langle n_2 \rangle = \left(N^l \frac{A_1 a_2 + m A_m a_2^m}{1 + A_1 a_2 + A_m a_2^m} \right) \left(\frac{A_1 + n A_n a_2^{n-1}}{1 + A_1 a_2 + A_n a_2^n} \right) \quad (18a)$$

Note that the second factor in Eq. (18a) was obtained by dividing Eq. (6b) by a_2 . Now we show that Eq. (18a) is inconsistent with the stepwise behavior. To do so, let us consider its behavior at large a_2 , in which the second factor of Eq. (18a) is dominated by

$$\frac{A_1 + n A_n a_2^{n-1}}{1 + A_1 a_2 + A_n a_2^n} \simeq \frac{n}{a_2} \quad (18b)$$

which is a decreasing function with a_2 . This means that Eq. (18a) cannot represent a multi-stepwise isotherm that converges, at large a_2 , to a saturating capacity. Thus, we have demonstrated that additive and multiplicative isotherms belong to different classes of sorption phenomena.

3.3. Connection to χ

Since isotherms are reported per unit sorbent quantity, it is defined under the constant n_1 ensemble. However, the standard measure of interactions in polymer science is the Flory χ , which quantifies net self-interaction, the self (i.e., segment-segment and sorbent-sorbent) minus mutual (segment-sorbent) interaction [47,79]. By assuming constant χ , sorption isotherms are of Type III. In

the fluctuation theory, Flory χ can be generalized using the Kirkwood-Buff integrals, as [80]

$$\chi = c_1 \left(G_{11}^{(\mu)} + G_{22}^{(\mu)} - 2G_{12}^{(\mu)} \right) \quad (19)$$

where c_1 is the concentration of species 1, and the Kirkwood-Buff integrals have been defined in the grand canonical ensemble (which has been emphasized by the superscript (μ)), unlike the *extended interfacial* Kirkwood-Buff integral $G_{22}^{(n_1)}$, which was defined under the constant n_1 condition in line with the practice for sorption isotherms (see Eqs. (3a) and (3b); here, the superscript was added for emphasis and distinction). Note that Eq. (19) is a model-free definition that does not pre-suppose the lattice model as in the case of Flory χ [47,81,82] and enables the calculation of this parameter even for systems out of thermodynamic equilibrium, that is for glassy polymers showing chiefly isotherms of Type II.

To relate our isotherm theory to χ , we need to convert the semi-open ensembles (constant n_1) to the grand canonical ensemble ($\{T, v, \mu_1, \mu_2\}$). This necessitates a relationship between the extended $G_{22}^{(n_1)}$ (under constant n_1) and χ . This can be achieved most straightforwardly by the statistical variable transformation (see Supporting Information G [83,84], which yields the following simple relationship:

$$\frac{N_{22}}{\langle n_2 \rangle} = - \left(\frac{\partial}{\partial a_2} \frac{a_2}{\langle n_2 \rangle} \right)_T = \chi + 1 \quad (20)$$

How χ changes with sorptive activity can be expressed through the derivation in Supporting Information G as

$$\chi = \frac{K a_2}{\langle n_2' \rangle} - (1 - K a_2) \left(\frac{1}{N} - \frac{1}{\langle n_2' \rangle} \frac{m(m-1)A_m a_2^{m-1}}{A_1 + m A_m a_2^{m-1}} \right) - 1 \quad (21)$$

where $\langle n_2' \rangle$, defined in Eq. (5b), was introduced for simplification. Using the fitting parameters in Table 4, we can show that χ is positive between the threshold activity and the completion of cooperative sorption (Fig. 5(a)). The calculated χ for methanol and 1-butanol converges above $a_2 > 0.4$ (Fig. 5(a)), where the isotherm rise comes exclusively from the Type III contribution (Fig. 4). The validity of this result is supported by the near-parallel $a_2/\langle n_2 \rangle$ in Fig. 5(b), whose gradient yields χ via Eq. (20). In the following, we shall refer to $N_{22}/\langle n_2 \rangle - 1$ calculated via Eq. (21) as χ . Yet, we emphasize here that the interpretation of $N_{22}/\langle n_2 \rangle - 1$ in terms of the χ with its meaning defined by the self- versus mutual-interactions (Eq. (19)) is possible only when sorbate and sorbent form a single phase.

For methanol and 1-butanol, χ exhibits a peak in the range of sorptive activity in which the dominantly cooperative isotherm (Fig. 5(a)). Swelling measurements for methanol in PTMSP show that the relative volume change is virtually zero in this region [33]. This suggests that the sorbate-sorbate association is the driving force for the positive χ , which takes place to fill the free volume in the membrane polymer without forming a strong sorbate-sorbent interaction. Note that the behavior of χ at low a_2 may be inaccurate as seen from Fig. 5(b), the peak of χ should stretch to lower a_2 . In comparison to methanol, the cooperative contribution for 1-butanol sorption rises and saturates at lower a_2 (see Fig. 4(a)), which is consistent with the behavior of χ in Fig. 5(a). In both cases, the positive χ , in combination with the lack of swelling, points to the predominance of sorbate-sorbate self-association that indicate the adsorption

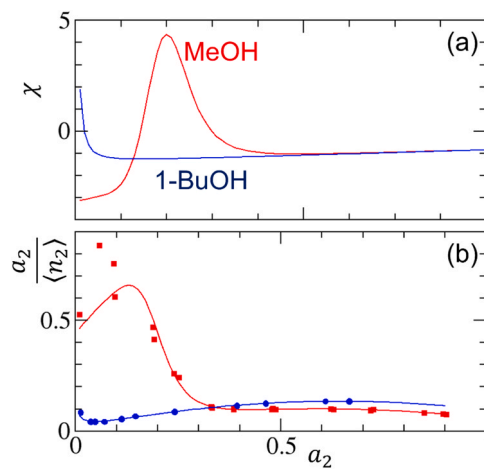


Fig. 5. (a) χ for alcohol sorption on poly[(trimethylsilyl)propyne] (PTMSP) versus methanol (red curve) and 1-butanol (blue curve) activities, calculated from Eq. (21), using the parameters in Table 4. (b) A plot of $a_2/\langle n_2 \rangle$ versus a_2 , whose gradient, according to Eq. (20), is $-(\chi+1)$, rationalizing the convergence of the two curves in (a) at $a_2 > 0.4$. The experimental data (red squares for methanol and blue circles for 1-butanol) have been calculated from the same experimental data used for Fig. 3. For methanol at low a_2 , Eq. (20) deviates from experimental $a_2/\langle n_2 \rangle$ which does not affect the fitting of the isotherm ($\langle n_2 \rangle$) in Fig. 3. Note that the fitting inaccuracy at the lower a_2 region for methanol seen in (b); the peak of χ for methanol in (a) should, therefore, be located at a lower a_2 .

behavior. At higher a_2 , where the Type III sorption takes place, χ is negative, showing the dominance of the mutual (polymer-sorptive) interaction over the self (polymer-polymer and sorbate-sorbate), which points to the dissolution of sorptives into the glassy membrane. This tendency is consistent with the swelling observed for this region for methanol in PTMSP [33]. Thus, a consistent microscopic picture underlying the isotherm can be derived by combining swelling and sorption measurements with the help of statistical thermodynamics. In this region, a combination of χ with the Kirkwood–Buff theory for binary mixtures [13,14,85] would help separate the three Kirkwood–Buff integrals that constitute χ .

4. Conclusions

Free-volume voids in polymers can be classified as micropores. Consequently, gas (vapor) molecules sorb onto the inner surfaces and dissolve in the polymer phase. Although simplified models neglecting either (dis)solution or (ad)sorption provide meaningful descriptions for simple isotherms, such traditional models do not capture the sorption-solution duality.

The key to addressing the above difficulty comes from statistical thermodynamics. The ABC isotherm, derived directly from the fundamental fluctuation relationship, renders the BET and GAB parameters to the mono-, di-, and tri-sorbate interactions, capturing the molecular interactions underlying an isotherm. The ABC isotherm handles the sorption-solution dualism effortlessly through the mathematical analogy between sorption and solution at the fundamental level and can be applied to Types II and III isotherms alike. For instance, as we have demonstrated in Tables 1–3, Dual Mode Sorption, Flory-Huggins, and ENSIC models can be generalized and re-interpreted in the universal formalism of the ABC isotherm.

Isotherms with complex functional shapes, such as the sorption of alcohols on poly[(trimethylsilyl)propyne] (PTMSP) [31,32,55,56], posed challenges in the past yet can be successfully interpreted by our statistical thermodynamic approach. We have derived a novel approach to modeling complex sorption via isotherm multiplicativity that can be derived directly from the fundamental excess number relationship of the statistical thermodynamic fluctuation theory.

Thus, our statistical thermodynamic theory can provide a standard isotherm theory for sorption and solution and a strategy to combine simple isotherms via isotherm multiplicativity and additivity. A unified theory of sorption for both glassy and rubbery polymers has emerged founded on the fundamental relationship between number fluctuations and chemical potential derivatives. Moreover, the isotherm equations derived in this work have the form of analytic expressions that can be easily adopted.

CRedit authorship contribution statement

Nobuyuki Matubayasi: Investigation, Writing – review & editing. **Karel Friess:** Investigation, Writing – review & editing. **Ondřej Vopicka:** Formal analysis, Investigation, Writing – review & editing. **Seishi Shimizu:** Conceptualization, Formal analysis, Writing – original draft, Writing – review & editing, Investigation.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data Availability

No data was used for the research described in the article.

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Appendix A. Supporting information

Supplementary materials associated with this article can be found in the online version at [doi:10.1016/j.physa.2024.129753](https://doi.org/10.1016/j.physa.2024.129753).

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