



Thermodynamics of water interactions with human stratum corneum. II. Interpretation via the Guggenheim–Anderson–deBoer isotherm

Santosh Yadav^a, Stephen W. Thiel^{a,*}, Gerald B. Kasting^b, Neville G. Pinto^a

^aDepartment of Chemical and Materials Engineering, University of Cincinnati, Cincinnati, OH 45221-0012, USA

^bCollege of Pharmacy, University of Cincinnati Medical Center, Cincinnati, OH 45267-0004, USA

ARTICLE INFO

Article history:

Received 24 June 2008

Received in revised form 22 October 2008

Accepted 11 November 2008

Available online 27 November 2008

Keywords:

Adsorption isotherm
Entropy of sorption
Heat of sorption
Isothermal calorimetry
Sorption isotherm
Stratum corneum

ABSTRACT

Studies of adsorption on biologically derived materials typically include direct measurement of either the adsorption isotherm or the heat of adsorption, but not both. Simultaneous measurement of adsorption and heat of adsorption should provide a more reliable description of the material under study. In this context, an analysis of the thermodynamics of water sorption is presented and a multilayer heat of sorption equation is derived within the framework of the Guggenheim–Anderson–deBoer (GAB) model. This model is applied to the previously published data for water vapor sorption and heat of water vapor sorption on stratum corneum (SC) over a range of relative humidities. The GAB models effectively characterize both heat evolution and equilibrium mass uptake over a broad water activity range. The thermodynamic results suggest significant restructuring of the SC during the sorption process; the sorption data alone are not sufficient to identify this effect. The results of this study emphasize first, the importance of incorporating a multilayer approach with variable energies of interaction in modeling of water uptake by SC and second, the utility of correlating sorption and calorimetric data simultaneously.

© 2008 Elsevier Ltd. All rights reserved.

1. Introduction

Water adsorption and the thermodynamics of water adsorption play a key role in the processing of many biologically derived materials. For example, there has long been interest in the interaction of water with wool and hair keratins, due to the importance of these materials in textiles and personal care applications (Cassie, 1945; D'Arcy and Watt, 1970; Downes and Mackay, 1958; Li and Holcombe, 1992; Li and Luo, 1999; Morrison and Hanlan, 1957; Watt, 1960, 1964, 1980). Similarly, there is significant interest in the interaction of water with foodstuffs (Fasina et al., 1997; Marcos et al., 1997; Quirijns et al., 2005a,b; Velazquez et al., 2003). Adsorption properties are typically quantified through the adsorption isotherm and through energetic effects (both enthalpic and entropic). These energetic effects are often useful in understanding the fundamental phenomena underlying macroscopic effects, and are needed for tight optimization of large-scale processing operations that require controlling moisture levels or drying.

Direct measurements of the heat of adsorption are rarely accompanied by simultaneous determination of the adsorption isotherm. It is quite common to quantify the energetic effects of sorption

using the isosteric heat of adsorption (Sircar, 2007), by measuring adsorption isotherms at several temperatures and applying the Clausius–Clapeyron equation to calculate the enthalpy of adsorption. For biologically derived materials, this approach is often complicated by the conformational and structural changes induced by water adsorption and temperature changes. The simultaneous measurement of the adsorption isotherm and the heat of adsorption overcomes this difficulty, as well as the limitations of the use of the Clausius–Clapeyron equation (Yadav et al., 2007).

In this context, the human stratum corneum (SC) is useful as a model system to study water interactions with biologically derived materials. The SC is a major barrier to the absorption into the circulation of most substances that are deposited on the skin surface. This barrier is essential to maintain physical and chemical equilibria with the environment. Since the SC is the rate-limiting diffusional barrier for most compounds, excised SC or skin sections containing SC are often used in determinations of the rate and extent of dermal absorption. Studies of water sorption (Anderson et al., 1973a,b; Blank, 1952; El-Shimi and Princen, 1978a; El-Shimi et al., 1975; Kasting and Barai, 2003; Leveque et al., 1987; Spencer et al., 1975; Yadav et al., 2007) and diffusion (Blank et al., 1984; Bouwstra et al., 1991; Bull, 1944; El-Shimi and Princen, 1978b; Kasting et al., 2003; Potts et al., 1991; Stockdale, 1978) in the SC have been published by various groups. The equilibrium sorption of water on SC follows a type II or type III isotherm, with a small amount of water sorbed at

* Corresponding author. Tel.: +1 513 556 4130; fax: +1 513 556 3474.

E-mail address: Stephen.Thiel@uc.edu (S.W. Thiel).

lower relative humidity (RH), and a relatively large amount of water sorbed at higher RH (Anderson et al., 1973a,b; Blank, 1952; El-Shimi and Princen, 1978a; El-Shimi et al., 1975; Kasting and Barai, 2003; Leveque et al., 1987; Spencer et al., 1975).

Kasting and Barai (2003) interpreted water vapor sorption data on SC from six laboratories using the Brunauer–Emmett–Teller (BET), D’Arcy–Watt, and Frenkel–Halsey–Hill (FHH) isotherms. The BET isotherm was modified to account for the finite water sorption observed when the gas phase was saturated with water vapor; otherwise, the BET isotherm describes the water sorption isotherm of human SC only below a water activity of 0.5 (Blank, 1952). A modified version of the FHH model (Kasting and Barai, 2003) and D’Arcy–Watt model (El-Shimi and Princen, 1978a; Kasting and Barai, 2003) successfully described the water sorption isotherm of human SC. The D’Arcy–Watt model has up to five parameters, and considers vapor-phase interactions with heterogeneous sorbents (D’Arcy and Watt, 1970; El-Shimi and Princen, 1978a; Kasting and Barai, 2003; Watt, 1980), while the FHH model includes long-range interactions between the sorbate and the sorbent, and assumes that the potential energy of the sorbate–sorbent interaction varies as the inverse n th power of the separation distance. The value of n varies between 2 and 3 for many systems (Adamson, 1976; Kasting and Barai, 2003). The parameters used in these models are linked to energetic interactions, but they have been determined in the cited studies purely by fitting the water sorption isotherms.

The results obtained by Kasting and Barai (2003) highlight two key aspects of the process by which water adsorbs onto SC. First, sorption clearly involves primary sorption of water onto active sites within the SC and subsequent adsorption of less tightly bound water in secondary layers. Second, the properties of the water bound in the secondary layers are influenced significantly by the presence of the SC. This second result invalidates one of the assumptions involved in the derivation of the BET isotherm, that the properties of water in the secondary layers are equivalent to the properties of liquid water. These results are consistent, however, with the assumptions used to develop the Guggenheim–Anderson–deBoer (GAB) isotherm, which is an extension of the Langmuir and BET adsorption models (Fasina et al., 1997; Marcos et al., 1997; Pradas et al., 2004; Pudipeddi et al., 1996; Quirijns et al., 2005a,b; Velazquez et al., 2003). In addition, the parameters of the GAB isotherm have clear thermodynamic interpretations that can be used to understand more completely the sorption process.

The present study couples the energetics of water interactions with SC with the sorption isotherm to provide insight into the sorption process; this is perhaps the first study reporting the simultaneous analysis of sorption and calorimetry data using the GAB isotherm. A multilayer heat of sorption equation is derived for the GAB model; this equation is then used in conjunction with the GAB water vapor sorption equation to obtain model coefficients. This model is used to characterize water uptake and heat of sorption on SC measured by isothermal microcalorimetry (Yadav et al., 2007). These results are used to infer structural changes during the sorption process (Kasting and Barai, 2003). The broader implications of the approach presented here are also discussed.

2. GAB adsorption isotherm and thermodynamics

2.1. Adsorption isotherm

The GAB isotherm is an extension of the Langmuir and BET adsorption models (Fasina et al., 1997; Marcos et al., 1997; Pradas et al., 2004; Pudipeddi et al., 1996; Quirijns et al., 2005a,b; Velazquez et al., 2003). It is based on the assumption of multilayer physical adsorption onto an adsorbent surface with active sites that are identical, distinguishable, and independent (Fasina et al., 1997; Marcos et al.,

1997; Quirijns et al., 2005a,b; Velazquez et al., 2003). The isotherm does not account for lateral interactions between molecules (Quirijns et al., 2005a,b). The development of the isotherm traditionally accounts for three types of adsorbed molecules: molecules adsorbed directly on the adsorbent surface, which are strongly influenced by interactions with the surface; molecules adsorbed in the next several layers (the *multilayer*), which are influenced less significantly by interactions with the adsorbent surface; and layers beyond the multilayer, which have properties identical to those of the adsorbate in bulk liquid form.

Based on these assumptions, the traditional form of the GAB sorption isotherm is obtained (Marcos et al., 1997; Pradas et al., 2004; Velazquez et al., 2003) as

$$\theta = \frac{Ckx}{(1-kx)(1-(1-C)kx)} \quad (1)$$

Eq. (1) relates the fractional coverage, θ , to the adsorbate activity, x , through the parameters, C and k . The natures of the parameters C and k , which are related to the thermodynamics of the adsorption process, are discussed in detail below. The fractional coverage is defined as

$$\theta = \frac{n}{n_m} \quad (2)$$

where n represents the moles adsorbed and n_m represents the moles adsorbed at monolayer coverage (one adsorbate molecule per adsorption site).

Pradas et al. (2004) developed Eq. (1) using a classical thermodynamic argument, modeling the adsorption process as a set of reactions in which i adsorbate molecules (B) associate with one adsorption site ($X0$) to form the complex XiB :



At equilibrium, the chemical potentials are related by

$$\mu_{XiB} = \mu_{X0} + i\mu_B \quad (4)$$

The chemical potential of the unassociated sites can be expressed as

$$\mu_{X0} = \mu_{X0}^0 + RT \ln \theta_0 \quad (5)$$

where

$$\theta_i = \frac{n_i}{n_m} \quad (6)$$

n_i is the number of complexes XiB , R is the gas law constant, T is the absolute temperature, and the superscript 0 denotes a property at standard state; n_0 is number of unoccupied adsorption sites. The chemical potential of the unassociated adsorbate can be written as

$$\mu_B = \mu_B^0 + RT \ln x \quad (7)$$

The chemical potential of complex XiB can be expressed as the sum of contributions from the first adsorbed layer and the multilayer:

$$\mu_{XiB} = \mu_{XB}^0 + (i-1)\mu_B^* + RT \ln \theta_i \quad (8)$$

where the superscript * indicates a property of the multilayer.

The GAB isotherm, Eq. (1), follows directly from these assumptions (Pradas et al., 2004); the following relationships are also obtained:

$$\theta_i = C\theta_0(kx)^i \quad (9)$$

$$C = \exp\left(\frac{\mu_B^* - \mu_{XB}^0}{RT}\right) \quad (10)$$

Download English Version:

<https://daneshyari.com/en/article/158099>

Download Persian Version:

<https://daneshyari.com/article/158099>

[Daneshyari.com](https://daneshyari.com)