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## Thermodynamic Estimate of the Number of Solvent Molecules Displaced by a Solute Molecule for Enthalpy-Driven Adsorption: Phenobarbital and Activated Carbons as the Model System

Peng Yu, Dale Eric Wurster\*

Division of Pharmaceutics and Translational Therapeutics, College of Pharmacy, University of Iowa, Iowa City, Iowa 52242

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## ABSTRACT

A Modified Crisp Equation, describing the differential Gibbs free energy of the adsorption process, is being proposed, which considers multiple sites available on the surface for adsorption and their relative fractions. The differential Gibbs free energy can be calculated by the van't Hoff Equation, which depends on the affinity constant in the Langmuir-like equation. To consider the number of solvent molecules displaced by a solute molecule in the adsorption process, a new derivative of the Langmuir-like equation is being proposed as well. By comparing the differential Gibbs free energies obtained from the 2 thermodynamic relationships, it can be determined that a phenobarbital molecule displaces 5 water molecules on the activated carbon surface for site-specific adsorption from solution. For the series of experimental conditions studied, including 4 activated carbons, pH effects, temperature effects, and solvent effects, the corrected differential Gibbs free energies using  $n_1 = 5$  for site-specific adsorption are quite consistent between the 2 thermodynamic relationships. The difference between the estimates of the differential Gibbs free energies by the Modified Crisp Equation and the van't Hoff Equation provides a new experimental method to calculate the number of solvent molecules displaced by an adsorbing solute molecule.

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## Introduction

Adsorption is a common phenomenon in both medicine and pharmaceutics,<sup>1</sup> which plays a critical role in physical and chemical stability of formulations,<sup>2–4</sup> surface analyses of pharmaceutical materials,<sup>5,6</sup> pharmaceutical disperse systems,<sup>7</sup> water treatment of pharmaceutical residues,<sup>8–10</sup> treatments of intoxications<sup>11,12</sup> and so on. It is, therefore, important to fully understand adsorption processes to better predict the outcomes. Adsorption of solute from solution is a displacement process, differing from that in the vapor phase. The Langmuir-like equation (LLE)<sup>13,14</sup> is widely used to describe adsorption isotherms in solution. It assumes that an adsorbing solute molecule displaces a certain number ( $n_1$ ) of solvent molecules on the surface. However, in the general expression of the LLE,  $n_1$  solvent molecules are treated as an ensemble to reach a 1:1 ratio between solvent and solute. This does not reflect the real

relationship between solvent and solute molecules involved in the adsorption-from-solution process. Thus, it is of great interest to estimate the number  $n_1$ , which can contribute to the accurate estimation of the energy change for the adsorption process.

Activated carbons are widely used in adsorption studies because of their beneficial surface properties.<sup>15,16</sup> The large specific surface areas of activated carbons lead to large capacities for different adsorbates. These large capacities simplify method development as well, by significantly changing free adsorbate concentrations. Activated carbons also have several different oxygen-containing functional groups on their surfaces.<sup>17–19</sup> Thus, they can interact with a wide variety of different adsorbates.

Phenobarbital is used to control seizures, relieve anxiety, and prevent withdrawal symptoms.<sup>20,21</sup> The structure of phenobarbital is shown in Figure 1. It has a polar barbituric acid ring and a nonpolar phenyl ring. The study of phenobarbital adsorption by activated carbons has both clinical overdose and pharmaceutical application.<sup>11,12,22</sup> Therefore, phenobarbital was selected as the model compound for further analysis of the adsorption process on the activated carbon surface.

In the present study, thermodynamic properties of the site-specific adsorption of phenobarbital from solution by the

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\* Correspondence to: Dale Eric Wurster (Telephone: (319) 335-2137; Fax: (319) 335-9349).

E-mail address: [dale-e-wurster@uiowa.edu](mailto:dale-e-wurster@uiowa.edu) (D.E. Wurster).

### Nomenclature

$n_2^s$	the amount of solute adsorbed on the surface
$m$	the mass of adsorbent
$C_{eq}$	the equilibrium concentration of solute in the bulk solution
$K_{HB}$	the capacity constant for non-site-specific adsorption
$K_1$	the affinity constant for site-specific adsorption
$K_2$	the capacity constant for site-specific adsorption
$\Gamma$	the amount of adsorbate per unit area of surface
$\tau$	an assumed surface thickness (5.4–6.6 Å)
$R$	the gas constant
$T$	the temperature
$\Delta\bar{G}$	the differential Gibbs free energy for adsorption
$A_0$	the limiting area occupied by a solute molecule on the surface
$C_{eq}^{0.5}$	the equilibrium concentration of solute in solution at 50% surface coverage
$p$	the average relative fractions of functional groups on the adsorbent surface
$A_{sp}$	the specific surface area
$a_1^s$	the activity of solvent molecules on the surface
$a_1^b$	the activity of solvent molecules in the bulk solution

$a_2^s$	the activity of solute molecules on the surface
$a_2^b$	the activity of solute molecules in the bulk solution
$K'$	the equilibrium constant
$\rho_{solvent}$	the density of the solvent
$MW_{solvent}$	the molecular weight of the solvent molecules
$MW_{solute}$	the molecular weight of the solute molecules
$K_1^{fraction}$	the fraction-based equilibrium constant
$x_1^s$	the fraction of solvent molecules occupying the surface
$x_2^s$	the fraction of solute molecules occupying the surface
$n_1$	the number of solvent molecules displaced by a solute molecule in the adsorption-from-solution process
$\Delta\bar{G}_{MC}$	the differential Gibbs free energy estimated by the Modified Crisp Model
$\Delta\bar{G}_{VH}$	the differential Gibbs free energy estimated by the van't Hoff model
$m_{solute}$	the moles of solute molecules in solution
$m_{solvent}$	the moles of solvent molecules in solution
$w_{solute}$	the weight of solute in solution
$w_{solvent}$	the weight of solvent in solution
$c_{solute}$	The concentration of solute in solution
$x_{solute}$	the fraction-based concentration of solute in solution

activated carbons were investigated. An estimation of the number of water molecules displaced by an absorbing phenobarbital molecule using thermodynamic relationships was conducted as well. The analyses developed are not specific to either activated carbons or phenobarbital.

### Materials and Adsorption Isotherm Description

#### Surface Properties of Activated Carbons

For the present study, 4 activated carbons were used as the model adsorbents. These were Super Char (lot G812R; Gulf Bio-Systems, Inc., Dallas, TX), Darco KB-B (lot J62260), Norit B Supra (lot 8003-4), and Norit U.S.P. XX (all from American Norit Company, Inc., Jacksonville, FL). A complete understanding and characterization of the surface is critical to any conclusions drawn about any adsorption process. For activated carbons, this includes the accurate

measurement of the specific surface area and the chemical composition of the surface.<sup>23,24</sup>

#### Specific Surface Area

The surface areas of the 4 activated carbon samples were measured by fitting the Brunauer–Emmett–Teller equation to nitrogen vapor adsorption data,<sup>19</sup> shown in Table 1.

#### Surface Composition

X-ray photoelectron spectroscopy has been used for characterizing the surface functionalities present on activated carbons.<sup>18,19,25,26</sup> Four functional states of carbon can be distinguished, which are hydrocarbon (C–C or C–H), hydroxyl or ether (C–OH or C–O–C), carbonyl (C=O), and carboxylic acid or ester (O=C–OH or O=C–O–C). Table 2 lists the average relative fractions of these functional states on the surfaces of the 4 activated carbons.<sup>19</sup> The presence of other oxygen-containing functional groups has been hypothesized on the activated carbon surface. However, these 4 appear to predominate. For the site-specific adsorption of phenobarbital from solution by activated carbons, the hydroxyl group acts as the adsorption site on the activated carbon surface.<sup>18</sup>

#### Isotherm Determination

Isotherm data were taken from previous studies.<sup>27,28</sup> A typical adsorption isotherm of phenobarbital by activated carbons from solution is shown in Figure 2.

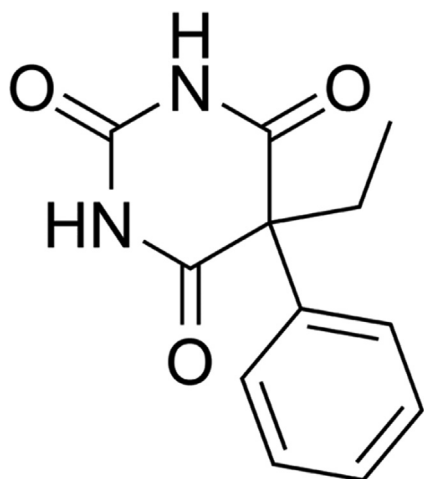


Figure 1. The structure of phenobarbital.

**Table 1**  
Specific Surface Areas of the 4 Activated Carbons as Determined by BET Analysis of Nitrogen Vapor Adsorption<sup>8</sup>

Activated Carbon	Specific Surface Area (m <sup>2</sup> /g)
Super Char	2950
Darco KB-B	1562
Norit B Supra	1350
Norit U.S.P. XX	995

BET, Brunauer–Emmett–Teller.

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