# Considerations about the correct evaluation of sorption thermodynamic parameters from equilibrium isotherms

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## ABSTRACT

This is a comparative analysis of popular methods currently in use to derive sorption thermodynamic parameters from temperature dependence of sorption isotherms. It is emphasized that the standard and isosteric thermodynamic parameters have sharply different meanings. Moreover, it is shown with examples how the sorption model adopted conditions the standard state and consequently the value of $\Delta G^\circ$ and $\Delta S^\circ$. These trivial but often neglected aspects should carefully be considered when comparing thermodynamic parameters from different literature sources. An effort by the scientific community is needed to define criteria for the choice of the standard state in sorption processes.

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## 1. Introduction

Sorption is a generic term covering the processes of adsorption, absorption and ion exchange [1]. Thermodynamic parameters of sorption processes, such as equilibrium constants, maximum sorption capacity and changes in entropies and enthalpies, give fundamental information on the mechanisms involved and are an essential requisite for the design and management of sorption/desorption plants.

Several techniques are employed to derive thermodynamic parameters of sorption processes; among the most popular, besides direct calorimetric measurements [2–4], is the measurement of isotherms at several temperatures, wherefrom both the standard and isosteric change of thermodynamic parameters can be derived.

Variations of standard thermodynamic parameters of sorption processes are referred to the transfer of a defined amount of substance (usually one mole) from solution onto the sorbent, with all chemicals involved in their standard state [5]. The standard states selected are absolutely essential for the interpretation of numerical values. On the contrary, the isosteric parameters refer to sorption at equilibrium [6].

The present paper analyzes popular methods in use to calculate sorption thermodynamic parameters from isotherms, utilizing data from the literature and data recorded in our own laboratory, with the aim of evaluating how the selected standard states affect the results. Attention is focused on sorption from liquid phase;

however, our conclusions are of general relevance and can easily be extended to sorption from gas.

## 2. Material and methods

Samples of immobilized humic acids and of a humic acids-zeolite adduct were prepared following the procedure described in detail elsewhere [7]. Shortly: a 1.0 mol dm$^{-3}$ CaCl$_2$ solution was added to a humic acid (HA, purchased from Sigma–Aldrich) solution until complete precipitation of humic substances as calcium humate (Ca-HA). After one day, the precipitate was collected by centrifugation and kept in an oven at 603 K for 1.5 h [8], in order to obtain an immobilized form of the HA salt (ImCaHA).

The organo-zeolite adduct (PCT-ImHA) was produced by binding HA to a zeolitic tuff rich in phyllipsite and chabazite [9], obtained from a quarry near Naples (Italy), and then heating the aggregate in an oven at 603 K for 1.5 h. The detailed chemical and mineralogical composition of the zeolitic tuff is reported in a previous work [9]. The organo-zeolite adduct, thanks to the ability of HA to bind organic compounds by hydrophobic interactions [10], is expected to efficiently sorb the compounds selected for this study. Zeolitic tuff surface is irrelevant to the sorption process itself, its only role being to immobilize the active HA [11].

For sorption tests, 20-cm$^3$ aliquots of o-xylene, cyclohexanol or toluene in aqueous TrisHCl/Tris buffer, $1.0 \cdot 10^{-3}$ mol · dm$^{-3}$, pH 7.0, concentration range 10–150 mg · dm$^{-3}$, plus 150 mg of the sorbent PCT-ImHA or 10 mg of the sorbent ImCaHA, were put in a glass container with a buthyl/PTFE cap and kept in a thermostat at the selected temperature with periodical shaking. After two

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days, 1.0 mm³ of supernatant was taken through the rubber cap and analyzed by gas chromatography. Analyses carried out after four and six days showed no further variation, indicating that sorption equilibrium was reached within the initial two days.

## 3. Thermodynamic background and analysis of sorption data

If the sorption process is entirely reversible, we can assume that thermodynamic equilibrium has been established and maintained over the entire concentration range. Each point of the sorption isotherm represents a specific sorbed state defined by one value of $q_e$, the amount of sorbate per unit mass (or volume) of sorbent, and one value of the equilibrium concentration in solution ($C_e$), or of the equilibrium partial pressure for sorption from gas.

At the equilibrium, the chemical potential of the sorbed form ($\mu^\sigma$) is equal to that of the free form in liquid phase ($\mu^l$):

$$\mu^\sigma = \mu^l. \tag{1}$$

For an infinitesimal change from one to another equilibrium state, we can write:

$$d\mu^\sigma = d\mu^l. \tag{2}$$

From this relation, the well-known van't Hoff equation can be derived:

$$\frac{d\ln(K)}{dT} = \frac{\Delta H^\circ}{RT^2}. \tag{3}$$

where $K$ is the equilibrium constant for the sorption interaction and $\Delta H^\circ$ the standard molar sorption enthalpy at temperature $T$. If we suppose that $\Delta H^\circ$ varies only slightly with the temperature over the temperature range of interest, the integration of (3) gives:

$$\ln(K) = -\frac{\Delta H^\circ}{R}\frac{1}{T} + Con. \tag{4}$$

where $Con$ is an integration constant.

The plot $\ln(K)$ against $1/T$ should be linear, and the slope equal to $-\Delta H^\circ/R$. Moreover using the relations:

$$\Delta G^\circ = -RT\ln(K). \tag{5}$$

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ, \tag{6}$$

the standard sorption energy ($\Delta G^\circ$) and the standard sorption entropy ($\Delta S^\circ$) can be calculated. Alternatively, $\Delta S^\circ$ can be derived directly from the plot $\ln(K)$ against $1/T$. Indeed, assuming that both $\Delta H^\circ$ and $\Delta S^\circ$ change only slightly with the temperature, we obtain:

$$\ln(K) = -\frac{\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R}, \tag{7}$$

where $\Delta S^\circ/R$ is the intercept on the ordinate.

### 3.1. Partitioning model

A particularly interesting and simple case, from the thermodynamic point of view, presents itself when the solute distributes between the solid and liquid phase [12–14] with a behavior similar to the partitioning between two immiscible liquid phases: the amount in the solid phase at the equilibrium ($q_e$) increases linearly with the equilibrium concentration in solution ($C_e$). As an example, the isotherms of o-xylene sorption onto immobilized humic acid (ImCaHA), recorded by us, show that the process follows the partitioning model at all temperatures tested (figure 1).
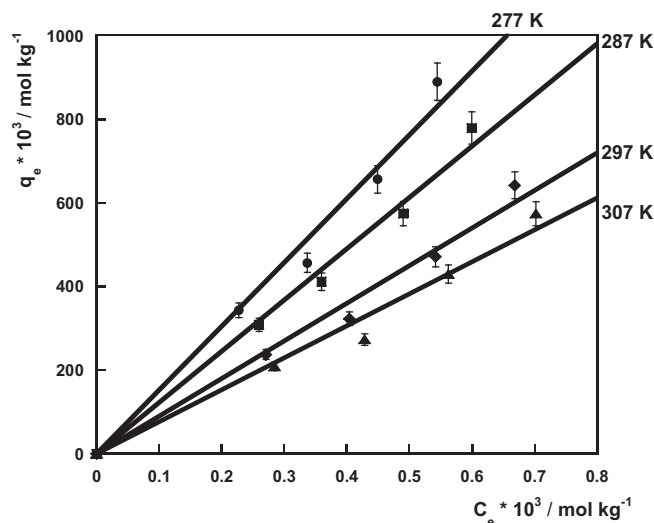
Let's consider the following equilibrium:

$$A(l) \rightleftarrows A(s), \tag{8}$$



**FIGURE 1.** Partitioning of o-xylene between ImCaHA and water at different temperatures.

$A(l)$ and $A(s)$ are the solute $A$ in the liquid phase and in the solid phase, respectively.

The equilibrium constant for this interaction is given by:

$$K_p = \frac{a_s}{a_l}, \tag{9}$$

where $a_s$ and $a_l$ are the activity of the solute in the solid phase and in the liquid phase. According to IUPAC indications for the Physical Chemistry quantities [15], the activity is a dimensionless quantity, therefore $K_p$ also is dimensionless.

Equation (9) is equivalent to:

$$K_p = \frac{\gamma_s \frac{C_s}{C_s^\circ}}{\gamma_l \frac{C_l}{C_l^\circ}}, \tag{10}$$

where $\gamma_s$ and $\gamma_l$ are the activity coefficients of the solute in solid phase and liquid phase, $C_s$ and $C_l$ are the concentrations in the two phases (solid and liquid), and $C_s^\circ$ and $C_l^\circ$ are the same in the selected standard states. For an ionic solute in a dilute solution, $\gamma_l$ can easily be computed by the Debye-Hückel limiting law [5]; moreover for a non-ionic solute at low concentration, $\gamma$ is $\approx 1$. Therefore, for a dilute solution of a non-ionic compound:

$$K_p = \frac{\frac{C_s}{C_s^\circ}}{\frac{C_l}{C_l^\circ}}. \tag{11}$$

Selecting the same standard state for the solute in the liquid and solid phase (for instance, 1 mol·L⁻¹, or 1 mol·kg⁻¹), and, consequently the same concentration measure units, we have:

$$K_p = \frac{C_s}{C_l}. \tag{12}$$

For ionic compounds, equation (12) should be integrated by the ionic strength effect on solute activity, according to the Debye-Hückel limiting law.

In line with equation (12), the slopes of the straight lines in figure 1 are the partitioning equilibrium constants. From equation (7), we calculated $\Delta H^\circ = -16.0 \pm 0.7$ kJ·mol⁻¹ and $\Delta S^\circ = 3.0 \pm 2.6$ J·mol⁻¹·K⁻¹ (figure 2).

These values are relative to the transfer of 1 mol of solute from a liquid phase with 1 mol·kg⁻¹ concentration to a sorbent with 1 mol·kg⁻¹ concentration, both displaying an ideal dilute behavior [5,15].