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Evaluation of surface excess isotherms in liquid chromatography

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ABSTRACT

Methods are proposed to calculate surface excess isotherms and to use them to derive adsorption isotherms in liquid chromatography. The consequences of these methods are discussed. The excess isotherm of isopropyl alcohol from its aqueous solutions on a C_{18} adsorbent was obtained using the minor disturbance method. The slope of the inflection tangent of the excess isotherm provides the position of the plane separating the adsorbed layer and the bulk phase, from which the adsorption isotherm was derived. At low concentrations of isopropyl alcohol, frontal analysis was used to derive the adsorption isotherm on the same adsorbent using an independent method. The isotherm was thus derived from both frontal analysis data and the minor disturbance method. The results obtained are compared. Our results show that the use of the same concentration unit for the calculation and the representation of the data is the only correct way to calculate the excess isotherms in practical applications of liquid chromatography.

1. Introduction

The interactions of liquids, gases, and vapors with solid adsorbents and the thermodynamic treatment of the phenomenon of adsorption were extensively studied during the last hundred years. The fundamental treatment by Gibbs [1] clarified the issues and lead to the definition of the excess quantities. The development and the applications of the Gibbs theory to study adsorption at solid/liquid interfaces were made by Kipling [2], Schay [3], and Everett [4,5]. In the field of liquid chromatography, the minor disturbance method has now become the most widely used method of measurement of the surface excess isotherm of the components of binary mixtures. The fundamentals of this method were first derived by Wang et al. [6]. The theoretical background was later discussed by Riedo and Kováts [7], which lead them to propose different approaches for the determination of the thermodynamic void volume of a chromatographic column [8].

Nowadays the minor disturbance method is widely used in liquid chromatography to determine the solvation process of adsorbent surfaces [9–11]. The data derived from this measurement has brought critical contributions to the modern understanding of the adsorption processes that take place in chromatographic columns.

There are several ways and conventions to calculate excess isotherms in liquid chromatography. It has been shown that the shape of the excess isotherms depends on the concentration unit used to calculate or represent excess adsorption [12,13]. The aim of this work is to compare different methods used for the representation of excess isotherms, to discuss their consequences, and to evaluate possible explanations arising from the different shapes and curvatures of these isotherms. The effect of the representation of excess isotherm data on the adsorption isotherms derived from these data will be analyzed. Finally we will compare these adsorption isotherm data with the isotherm derived from frontal analysis measurements and suggest the most accurate method of calculation of the excess isotherms.

2. Theory

2.1. Excess isotherm calculations

The minor disturbance method is widely used for the calculation of excess isotherms in liquid chromatography. This method consists in percolating the column with a binary mixture of the two compounds considered. When a steady-state equilibrium has been reached between the stationary phase and the stream of mixture, small perturbations of the mixture composition are caused by injecting an excess of one of the two compounds into the stream. This perturbation generates peaks, the retention volumes of which are measured. The experiment is repeated with mixtures of different compositions covering the whole range from one pure

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compound to the other. The disturbance method is also known as the perturbation method or the 'peak on a plateau' method [14]. By analyzing the relationship between the retention times of these peaks and the composition of the mixture used, the method provides the excess isotherm of each of the two compounds in the other one over the entire concentration range. The calculation uses the column mass balance equation, from which Kazakevich and McNair [15] derived the essential equation for the determination of excess isotherms in liquid chromatography.

The most widely used convention in liquid chromatography is based on the volume fraction of the studied component in the binary mixture. The calculation then characterizes the eluent composition by the volume fraction of one of the components of the binary mixture.

Let us define a binary mixture that consists of two completely miscible fluids, A and B. The amount of component A in a short cross-sectional layer of the chromatographic column is the sum of its equilibrium amount in the liquid free from the influence of the surface forces and of its surface excess:

$$v_0\phi_A + s\Gamma_A \tag{1}$$

where v_0 is the volume of the liquid phase and s is the surface area of adsorbent inside the column cross-sectional layer between lengths x and $x+dx$, ϕ_A is the volume fraction of component A in the bulk mixture, and Γ_A is its surface excess. Introducing the volumetric flow rate, F_v, through the cross-sectional layer, the column mass balance can be written:

$$-F_v\left(\frac{\partial \phi_A}{\partial x}\right)_t = v_0\left(\frac{\partial \phi_A}{\partial t}\right)_x + s\left(\frac{\partial \Gamma_A}{\partial t}\right)_x \tag{2}$$

Substituting the following equation to Eq. (2):

$$\left(\frac{\partial \Gamma_A}{\partial t}\right)_x = \left(\frac{\partial \Gamma_A}{\partial \phi_A}\right)_x \left(\frac{\partial \phi_A}{\partial t}\right)_x \tag{3}$$

results in

$$-F_v\left(\frac{\partial \phi_A}{\partial x}\right)_t = v_0\left(\frac{\partial \phi_A}{\partial t}\right)_x + s\left(\frac{\partial \Gamma_A}{\partial \phi_A}\right)_x \left(\frac{\partial \phi_A}{\partial t}\right)_x \tag{4}$$

since $(\partial\Gamma_A/\partial\phi_A)_x$ is the full derivative of the adsorption isotherm. We can write, after simplification:

$$-F_v\left(\frac{\partial \phi_A}{\partial x}\right)_t = \left(v_0 + s\frac{d\Gamma_A}{d\phi_A}\right)\left(\frac{\partial \phi_A}{\partial t}\right)_x \tag{5}$$

Using the properties of the partial derivatives, the last term on the right-hand side can be replaced by:

$$\left(\frac{\partial \phi_A}{\partial t}\right)_x = -\left(\frac{\partial \phi_A}{\partial x}\right)_t \left(\frac{\partial x}{\partial t}\right)_{\phi_A} \tag{6}$$

where the last term is the linear velocity of the chromatographic band at the given concentration:

$$u_{\phi_A} = \left(\frac{\partial x}{\partial t}\right)_{\phi_A} \tag{7}$$

After simplifications and rearrangement, and expanding the equation to the whole column by introducing L the column length we obtain:

$$u_{\phi_A} = \frac{F_v L}{V_0 + S((d\Gamma_A)/(d\phi_A))} \tag{8}$$

Since the retention volume of the disturbance peak $V_{R,A}(\phi)$ for a given volume fraction of the mixture is given by:

$$V_{R,A}(\phi) = \frac{F_v L}{u_{\phi_A}} \tag{9}$$

Replacing Eq. (9) to Eq. (8) results:

$$V_{R,A}(\phi) = V_0 + S\frac{d\Gamma_A}{d\phi_A} \tag{10}$$

Eq. (10) gives the expression for the excess amount calculation:

$$\Gamma_A = \frac{\int_0^1 (V_{R,A}(\phi) - V_0)d\phi_A}{S} \tag{11}$$

where the surface excess of component A of the binary mixture is in [cm^3/m^2], S is the surface area of the packing material contained in the column, and V_0 is the thermodynamic void volume calculated by:

$$V_0 = \int_0^1 V_{R,A}(\phi)d\phi \tag{12}$$

Note that the use of molar concentrations for the calculation of excess isotherms is based on volume fraction concentrations. In this case the concentration is given by the product of the volume fraction and the molar volume of the given component of the binary mixture [11,16]

2.2. The adsorption isotherm derived from excess isotherm

To estimate the total amount of the compound of interest adsorbed at equilibrium, a dividing plane has to be placed between the mobile and the stationary phases. In other words, we need to decide which fraction of the mobile phase in the column is under the influence of the adsorbent, in an adsorption layer, and which fraction belongs to the "bulk" phase. This decision is the most critical point of the derivation. The fundamental equations for the excess volume based on molar-fraction and on volume-fraction definitions of the concentration are derived as explained by Schay [3] and Kipling and Wright [17]. In the following section we will follow the derivation for the calculation of adsorption isotherms under static conditions. The extension and consequences of the conversion from moles to volume unit will also be discussed.

When a binary mixture is in contact with an adsorbent surface, the surface does not adsorb them in equal amounts but adsorbs one preferably to the other. Therefore, the adsorbed layer becomes more concentrated in that component than the bulk phase, which is not influenced by the surface forces. Accordingly, to express the difference of the concentrations of this component in the two phases in molar fraction, we let Δx_A be the concentration difference for the compound of interest, compound A in the binary mixture, after equilibration with the adsorbent surface. If we take a snapshot of the chromatographic column when equilibrium is reached, this concentration difference can be expressed as follows:

$$\Delta x_A = x_A^0 - x_A \tag{13}$$

where x_A^0 is the concentration of component A in the bulk liquid and x_A its concentration after equilibrium with the adsorbent surface has been reached. Δx depends on the adsorbent surface and on the total number of moles n^0 of compounds present in the column. With these definitions, the surface excess of component A in terms of moles and molar fractions is:

$$\Gamma_A^x = \frac{n^0 \Delta x_A}{S} \tag{14}$$

where S is the adsorbent surface area of the material in the column. The liquid phase in the column can be divided into two parts, depending on the influence of the adsorbent surface on the liquid phase:

$$n_0 = n^b + n^a S \tag{15}$$

where n^b is the number of moles contained by the bulk phase that are not influenced by the surface forces and n^a is the number of