



Modifier adsorption in supercritical fluid chromatography onto silica surface



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ABSTRACT

The adsorption of methanol, ethanol and isopropyl alcohol on a silicagel adsorbent from supercritical carbon dioxide was investigated using nonlinear chromatographic techniques. Series of adsorption isotherm data points of these alcohols were determined by frontal analysis. Their nonlinear adsorption behavior were modeled using a modified BET equation extended for heterogeneous adsorption surfaces. Our results suggest the formation of an adsorbed multilayer of alcohols above the silica surface. This organic solvent enriched layer governs the separation of the analytes in supercritical fluid chromatographic separations, both under analytical and preparative conditions.

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1. Introduction

The organic modifiers added to supercritical carbon dioxide may affect the chromatographic system in two ways. (1) Adding an organic solvent to carbon dioxide will increase the density of the mobile phase above that of pure carbon dioxide. (2) The organic modifier interacts in some ways with the adsorbent surface, depending on the nature of the solvent molecule and on the chemical structure of the column packing. This interaction strongly influences the accessibility by analyte molecules of the adsorption sites located on the surface. Janssen et al. [1] suggested that the second of these effects has a predominant influence on the peak shape and the column efficiency in practical supercritical fluid chromatography. These authors determined the adsorption isotherms of tetrahydrofuran, methanol, ethanol, and isopropyl alcohol on an octadecyl modified silica adsorbent. They modeled the adsorption data of these modifiers using a Langmuir isotherm and found that even the small addition of organic modifier can significantly improve the peak shape and the selectivity of separations carried out using supercritical carbon dioxide as the mobile phase. They related this effect to the deactivation of the residual polar groups on the adsorbent surface through the adsorption of the organic solvent molecules [2].

The interaction of small molecules with a silicagel surface was studied using various methods in the past decades. Scott and Kucera [3] showed that polar solvent molecules able to give hydrogen

bonding, such as isopropyl alcohol or ethyl acetate dissolved in n-heptane, interact with the silica surface by forming a monolayer at lower concentrations or an adsorbed double layer at higher concentrations. Lochmüller and Mink [4] measured the adsorption isotherm of ethyl-acetate on a silica adsorbent from supercritical carbon dioxide, and modeled the adsorption using the Langmuir isotherm model.

The adsorption of supercritical carbon dioxide on silica, chemically bonded C₁₈ silica and SE30 coated silica; and the binary isotherms of carbon dioxide and methanol chemically bonded C₁₈ silica and neat silica were described by Strubinger et al. [5,6]. Their results of CO₂ adsorption showed an increase of the adsorbed amount of carbon dioxide with increasing system pressure and with decreasing temperature in the supercritical region. Their study of the adsorption of binary mixtures showed similar results with a dramatic increase in the adsorbed amount of methanol around the critical pressure of carbon dioxide. The measurement of the hold-up time of a packed column operated with mixtures of organic solvent and liquid carbon dioxide has been discussed by Guardale et al. [7]. The effect of the organic modifier on the analyte retention has been determined by West and Lesellier [8] applying linear solvation relationships. The retention mechanism in supercritical fluid chromatography has been reviewed by Lesellier [9].

Accounting for the adsorption of organic modifiers in supercritical fluid chromatography has a critical importance in both preparative- and analytical-scale applications. The organic modifiers used in preparative supercritical fluid chromatography compete with the sample components for access to the adsorption sites, which may significantly affect the adsorption isotherms of these compounds. The proper thermodynamical modeling of this

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competition between solvent and components is fundamental to design and carry out economical and environmental friendly large scale purification and separation processes. Obviously, the nature of each analyte affects its retention properties under analytical conditions as well. Finally, the study of binary systems leads us to investigate the development of band fronts in Supercritical Fluid Chromatography during frontal experiments. It gives us insights on the effect of density changes of the supercritical mobile phase through packed columns on these properties. All these effects are keys to a more detailed understanding of the thermodynamics of Supercritical Fluid Chromatographic systems.

This paper examines the adsorption behavior of methanol, ethanol, and isopropyl alcohol on a silicagel column from supercritical carbon dioxide, using frontal analysis. The experiments were designed to explore the interactions between the silica surface and small polar organic modifier molecules. During the analysis of the frontal data, the detailed mapping of the surface adsorption centers will be considered and the multilayer formation of alcohols above the column bed will be proved.

2. Theory

2.1. Frontal analysis for isotherm determination

The physico-chemical properties of chromatographic adsorbents are often characterized by the results of frontal analysis [10,11]. The method consists in percolating the column with a known solution of the studied compound and in sharply increasing from time to time this concentration at the column inlet by a known amount, for a sufficiently long period of time. The result of the experiment is a frontal chromatogram, which is recorded at the column outlet. The abrupt change of inlet concentration results in a steep change in the outlet concentration, a front shock or front shock layer. Based on the properties of this front shock the adsorbed amount of the studied compound q at equilibrium between the mobile phase concentration C can be calculated using the following equation [12]:

$$q = \frac{C(V_{R,F} - V_{\text{sys.,pump-det.}} - V_0)}{V_a} \quad (1)$$

where $V_{R,F}$ is the retention volume of the front shock, $V_{\text{sys.,pump-det.}}$ is the volume of the connecting tubes, the mixing chamber and the detector cell of the chromatograph from the pump to the detector, V_0 is the void volume of the column, and V_a is the volume of stationary phase in the column tube.

2.2. Isotherm models

The isotherm model derived by Langmuir [13] is the most widely used model in adsorption studies to describe the ideal adsorption processes on homogeneous adsorption surfaces for a wide variety of adsorption systems. The isotherm equation determines the correlation between the adsorbed amount q of the compound of interest at its equilibrium concentration C , using two parameters:

$$q = \frac{aC}{1 + b_s C} \quad (2)$$

where a is the initial slope of the isotherm, or the Henry constant of the adsorption. The parameters a and b_s are related by:

$$a = q_s b_s \quad (3)$$

where q_s is the monolayer saturation capacity of the adsorbent and b_s is the related adsorption equilibrium constant.

An extension of the Langmuir model for nonideal systems was derived by Brunauer, Emmett and Teller [14]. Their isotherm equation

gives the physical description of Type II and Type III. [15] adsorption isotherms. This isotherm equation describes the nonideal adsorption behavior of a compound on a homogeneous surface. This equation can be extended to liquid–solid adsorption systems [12,16]:

$$q = \frac{aC}{(1 - b_l C)(1 - b_l C + b_s C)} \quad (4)$$

where b_l is an additional adsorption equilibrium constant added to the Langmuir equation to take into account the interaction between the adsorbed molecules themselves. If the phase ratio F is known, the retention factor k for homogeneous adsorption surfaces is given by:

$$k = Fa \quad (5)$$

All adsorbents used in the practice of liquid chromatography are heterogeneous. In some cases this heterogeneity can be observed during the experimental process, in some cases this property remains hidden [17]. If the surface can be considered as made of two independent types of adsorption sites, Eq. (2) can be extended to take the heterogeneity into account. The resulting equation is built up from two Langmuir-term:

$$q = \frac{a_1 C}{1 + b_{s,1} C} + \frac{a_2 C}{1 + b_{s,2} C} \quad (6)$$

where a_1 and a_2 are the initial slopes of the isotherms determined on the two sets of independent adsorption sites with the two corresponding adsorption equilibrium constants $b_{s,1}$ and $b_{s,2}$. In some cases, interactions can take place above a heterogeneous surface between adsorbed molecules. In this case, the adsorption equilibrium constant describing this phenomena b_l can be assumed to be independent of the surface forces, and the BET equation can be extended to heterogeneous surfaces:

$$q = \frac{a_1 C}{(1 - b_l C)(1 - b_l C + b_{s,1} C)} + \frac{a_2 C}{(1 - b_l C)(1 - b_l C + b_{s,2} C)} \quad (7)$$

The retention factor of a compound on a heterogeneous surface is given by the contribution of the two independent adsorption site:

$$k = (a_1 + a_2)F \quad (8)$$

2.3. Adsorption energy distribution

Once the adsorption energy distribution has been calculated, it is possible to derive estimates of the degree of surface heterogeneity to determine the isotherm parameters, based on the use of raw isotherm data points, thus using an approach independent of the other methods of determination of these parameters. The calculation of the adsorption energy distribution provides support in the choice of the isotherm model between those suggested by the comparison of nonlinear fits of different isotherm equations to the experimental data points derived from frontal analysis measurements.

The adsorption energy distribution can be calculated for gas–solid systems by solving the following integral:

$$q(P) = \int_0^\infty f(\epsilon) \Theta(\epsilon, P) d\epsilon \quad (9)$$

where $q(P)$ is the amount of solute adsorbed at equilibrium with the solute partial pressure P , $f(\epsilon)$ is the adsorption energy distribution, $\Theta(\epsilon, P)$ is the local model of adsorption, and ϵ is the adsorption energy. The local model of adsorption is the isotherm model that describes the adsorption on the actual homogeneous patch of adsorbent. The extension of Eq. (9) to liquid–solid system requires the introduction of the equilibrium concentration. According to the previous section we have two basic choices. We

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