Non-equilibrium effects in liquid-solid chromatography and flow sorption microcalorimetry

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Abstract: Several flow techniques were studied to obtain adsorption and enthalpy data at liquid/solid interfaces. n-Butanol (solute), water (solvent) and graphitized Printex-300 carbon black (adsorbent) were selected for use. Adsorption and desorption paths in the one-step and step-by-step (cumulative) methods were investigated. Although the adsorption-displacement process was found to be reversible in nature, the adsorption and enthalpy curves of the one-step method eventually lie well above or below the corresponding cumulative isotherms due to non-equilibrium effects occurring in the one-step experiments.

Key words: Adsorption from solution; liquid chromatography; enthalpy of displacement; flow calorimetry

Introduction

The flow technique proved to be a powerful method for the investigation of adsorption phenomena at solid/solution interfaces. During the flow replacement experiment, a stream of pure liquid or of a solution is percolated through a column loaded with the adsorbent. In the one-step method the column inlet is switched to solutions of increasing concentration, starting from pure solvent in each case (adsorption path), which is followed by elution with pure solvent (desorption path). The step-by-step (cumulative) method is based on a finite sequence of closely spaced concentrations, starting from pure solvent initially (adsorption path); measurements are then made in the reverse direction (desorption path). If the solid sample is held in a chromatographic column and the outlet concentrations are continuously monitored and recorded by a detector, the adsorption excess isotherm (mass exchange) can be deduced from the breakthrough curves (flow frontal analysis liquid-solid chromatography, LSC). If the sorption vessel of a flow microcalorimeter is used as the adsorption column, the enthalpy isotherm of displacement (heat exchange) can be obtained (flow sorption microcalorimetry, FSM). In a more sophisticated procedure (which involves some practical difficulties), the detector is connected to the exit port of the calorimeter (on-line fit); hence, LSC and FSM measurements are made simultaneously on the same solid sample. In LSC, the one-step method has been applied by, among others, Sharma and Fort [1], while the cumulative method was preferred by Wang et al. [2] and Koch et al. [3]. In FSM, both methods were used by Findenegg et al. [4] and Woodbury and Noll [5]. Simultaneously LSC and FSM experiments were performed by Jednacak-Biscan and Pravdic [6, 7], Noll and Burchfield [8] and Denoyel et al. [9]. Questions arise of whether the one-step and step-by-step methods lead to the same adsorption and enthalpy isotherms and how they correlate with the corresponding immersion experiments. Different calorimetric protocols led to different enthalpy isotherms [4, 5, 10], and efforts have been made to convert one of them to another [5]. Mixing between surface and bulk phases, mixing at the interface between replacing and replaced solutions, and non-equilibrium (kinetic) effects were considered to be the most likely reasons for such differences [5]. To obtain adsorption excess isotherms, it has been concluded that flow frontal analysis LSC is not restricted to instantaneous equilibrium chromatography [2]. Glückauf's method is based on the special evaluation of a single, high-step elution chromatogram. When it
was applied, however, non-equilibrium effects were found to play an important role and a correction procedure was presented to eliminate them [11]. It may be inferred from the above-mentioned dynamic studies that a careful analysis of the methodology and experimental conditions should precede any theoretical conclusions drawn from the experimental results. The aim of this paper is to compare the adsorption and thermal data obtained from various flow methods and to interpret them solely from an experimental point of view.

Theoretical background

A schematic diagram of the experimental design, applicable to simultaneous FSM and LSC measurements, is shown in Fig. 1. The apparatus consists of a set of liquid sample holders, two pumps, and a six-way valve to select the liquid sample of interest, the sorption vessel of the microcalorimeter, and a connected analytical device (e.g., a differential refractometer) supplied with a recorder. Theoretical (ideal) and experimental chromatograms are presented in the schematic Fig. 2. The distribution function of the concentration, $F(t)$, is recorded continuously as a function of time $t$. The corresponding density function is

$$f(t) = \frac{dF(t)}{dt}.$$  \hspace{1cm} (1)

The extent of the system is defined as starting at the selection valve and ending at the detector. The liquid flow begins at $t_0$ and terminates at $t_\infty$, after which a solution of new composition is started. The dead volume of the system $V_D$ is the sum of the volumes of the tubing and fittings and the void volume of the column. If the volumetric flow rate $Q$ is maintained constant, the dead time can be calculated as

$$t_D = \frac{V_D}{Q}. \hspace{1cm} (2)$$

The experimental quantity $t_R$ is referred to as the retention time. It is located on the time scale at the point where the two shaded areas in Fig. 2 are equal. It can be expressed as a mean value:

$$t_R = \frac{1}{t_0} \int_{t_0}^{t_\infty} t f(t) dt = \int_{t_0}^{t_\infty} f(t) dt. \hspace{1cm} (3)$$

![Fig. 1. Experimental design for a simultaneous calorimetric-chromatographic assay of adsorption in solid/binary liquid systems](image1.png)

![Fig. 2. Concentration distributions and the corresponding (probability) density functions for ideal (Figs. 2a and 2b) and experimental (Figs. 2c and 2d) chromatography](image2.png)