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Expanding the elution by characteristic point method for determination of various types of adsorption isotherms

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ABSTRACT

Important improvements have recently been made on the elution by characteristic point (ECP) method to increase the accuracy of the determined adsorption isotherms. However, the method has so far been limited/used for only type I adsorption isotherms (*e.g.* Langmuir, Tóth, bi-Langmuir). In this study, general strategies are developed to expand the ECP method for the determination of more complex adsorption isotherms including such containing inflection points. We will exemplify the methodology with type II, type III and type V isotherms. Guidelines are given for how to determine such isotherms using the ECP method and for the experimental considerations that must be taken into account or that may be eliminated in the particular case.

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1. Introduction

The determination of proper adsorption isotherm data is important for a wide range of communities in chemistry except the chromatographic communities. Liquid chromatography [1,2] and gas chromatography [3,4] are reliable methods for detailed investigations and characterizations of the energy involved in solid–liquid interactions and solid–gas interactions, respectively. A thermodynamic understanding of the surface energy is also important in any industrial processes involving interactions with surfaces such as coating, wetting, agglomeration of solids, powder handling, dispersion of liquids and catalysis. From adsorption isotherms a wide variety of information – important for researchers' in academy and industry – can be achieved using a standard HPLC equipment, such as the characterization of polymers, pharmaceutical solids, and characterizations of new materials based on physical-chemistry and surface analysis [1–4].

Adsorption isotherms are most important also for the chromatographic communities; the data contains the key-information required for computer-assisted optimizations of preparative chromatographic systems [5]. New and better methods for the investigation of adsorption isotherms are therefore of prime importance for predicting the optimal conditions of a particular preparative separation. But the study of the adsorption isotherms in a phase system is also essential for a deeper understanding of the thermodynamics of the adsorption processes in the particulate chromatographic system [5–7]. The only way so far to investigate the retention mechanism in separation systems comprising of several types of adsorption sites is by isolating them through the modeling of the actual adsorption isotherms [6]. In fact pure homogenous systems, regarding the adsorption energy, are not frequently found [8]. In most separation systems, the solute adsorption is described with type I adsorption isotherms, i.e. isotherms that are convex upwards. These isotherms can comprise of one (*e.g.* Langmuir) or several different adsorption sites (*e.g.* bi-Langmuir). In many cases, the solute adsorptions to phase systems are best described by more complex types of adsorption isotherms. In other cases, such as in the adsorption of the simple neutral component ethylbenzene on C_{18} (ODS) column and the adsorption of charged solutes where the pH of the eluent is close to the solutes pK_a-value, the corresponding adsorption isotherms can deviate much from type I behavior [8,9]. Gas–solid adsorption isotherms have been divided into six classes according to their shapes [10,11]. The most common type I adsorption isotherm (Langmuir or similar) is convex upwards and reaches a limiting surface capacity. The type III adsorption isotherm has instead a concave upwards shape and is sometimes called anti-Langmuir. The type II, type V and VI are more complex and contains at least one inflection point.

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Frontal analysis (FA) is considered one of the most accurate methods for adsorption isotherm determination and can be used for "any" type of adsorption isotherm [5]. However, FA is both tedious and time-consuming. The elution by characteristic point (ECP) method is a much faster method but the method has only been developed/used for determination of type I adsorption isotherms [7,12–18]. In the ECP method, the adsorption isotherm is classically generated by integrating the concentrations retention volume from the diffuse back of an overloaded profile. The reason why the ECP method has not been used for determination of adsorption isotherms with inflection points before, is probably that elution profiles based on such isotherms does not contain any continuous diffuse parts over the whole concentration range.

The ECP theory is derived using the ideal model assuming infinite column efficiency while the efficiency of a real column is finite. This results in an unavoidable and inherent error in the derived isotherms. However, the size of this error decreases considerably with increasing number of plates (N) [16,17]. For Langmuir models $N > 2000$ is required for an error smaller than 3% [16] and for bi-Langmuir models $N > 5000$ is required for an error smaller than 5% [17]. Another reason for the lower accuracy of the ECP method as compared to the FA method is that the ECP theory assumes rectangular injection profiles [19]. This leads to large errors, since generally when the ECP method is used, it is necessary to inject very large volumes, leading to extremely tailed rears of the injection profiles deviating extremely from rectangular shapes [19,20]. This important source of error was recently more or less completely "eliminated" by a technical improvement called the ECP-CUT method [19]. Here, a sharp slice was made on the rear of the injection zone before it exited the injection loop by returning the position of the injector valve to load at an exact time before the remaining content of the loop has reached the column top. The adsorption isotherms generated applying the ECP-CUT method nearly totally coincides with the corresponding adsorption isotherms using the FA method [19]. In another recent study, the systematic error caused by the selection of the integrating starting point at concentration equal to 0 was reduced by replacing the classical integration with the use of raw slope data [21]. This also allows excluding extreme low concentration data, which are more affected by the separation systems limited efficiency. After this modification it is no longer required that the elution profiles contain continuous diffuse parts.

The aim of the study is to develop and demonstrate a new approach to generate adsorption isotherm data from adsorption isotherms deviating from type I using an expanded ECP methodology. We are going to limit our investigation to models with maximum one inflection point (i.e. types II, III and V). However, the principles presented could be applied to any case with several inflection points as will also briefly be discussed.

2. Theory

2.1. Elution by characteristic method (ECP)

This section comprises a theoretical background for understanding how the elution by characteristic point (ECP) method can be used for determination of adsorption isotherms deviating from type I. In this study we limit our discussion to only very large injection volumes, so that a concentration plateau is established.

The elution zone of a solute with a type I adsorption isotherm behavior has a sharp front and a diffuse rear. Each concentration in the rear has a unique elution (retention) volume according to:

$$V_R(C) = V_{inj} + V_0\left(1 + \frac{V_a}{V_0}\frac{dq}{dC}\right), \quad (1)$$

where $V_R(C)$ is the elution volume corresponding to the mobile phase concentration C. V_{inj} is the injected volume, V_0 is the hold-up volume, V_a is the stationary phase volume and dq/dC is the slope of the adsorption isotherm. An elution zone of a solute with a type III adsorption isotherm behavior has an "opposite" shape; now the front is diffusive and the rear is sharp. Thus, the retention volumes of the diffuse part will now be independent on the injection volume (V_{inj}) according to below.

$$V_R(C) = V_0\left(1 + \frac{V_a}{V_0}\frac{dq}{dC}\right) \quad (2)$$

Classically elution by characteristic point (ECP) method for type I adsorption isotherms are generated by integrating the rear of the elution zone:

$$q(C) = \frac{1}{V_a}\int_0^C (V_R(C) - V_{inj} - V_0)dC \quad (3a)$$

Integration of the profiles requires that the adsorption isotherm does not contain any inflection points and that the integration part is continuous. It also requires that the integration can start at concentration zero. For type III as we stated above V_{inj} is excluded resulting in:

$$q(C) = \frac{1}{V_a}\int_0^C (V_R(C) - V_0)dC \quad (3b)$$

Instead of integrating the diffuse part of the profile one can also use the raw slope of the adsorption isotherm [21]. For type I adsorption isotherm this is achieved by rewriting Eq. (1) to below:

$$\frac{dq(C)}{dC} = \frac{V_R(C) - V_{inj} - V_0}{V_a}, \quad (4a)$$

and in the case of a type III adsorption isotherm:

$$\frac{dq(C)}{dC} = \frac{V_R(C) - V_0}{V_a}. \quad (4b)$$

Eq. (4a) is nearly an identical expression to the one used to determine the adsorption isotherms using the perturbation peak (PP) method [22,23]; the only difference being that instead of V_{inj} one uses $V_{inj}/2$. The PP method is a method based on a set of different feed concentrations throughout the concentration range of the adsorption isotherm. On each feed concentration plateau of the solute, a small injection (usually so small that $V_{inj}/2$ could be excluded) causing a small disturbance of the equilibrium is performed. The small peaks generated will have different retention volumes time related to the tangential slope of the adsorption isotherm at that actual plateau feed concentration making it possible to describe the whole adsorption isotherm.

2.2. Principles for expanded use of ECP

An important rule for the relation between the curvature of the adsorption isotherm and the shapes of the different parts of the concentration bands has been outlined earlier [24,25], see in particular the illustration of the principle in Fig. 1 in Zhang et al. [24]. Operational lines for an adsorption step from an established concentration plateau of C_0, to a new higher concentration plateau of C_{inj} ($C_{inj} > C_0$) or for a desorption step going from C_{inj} back to C_0 are given by the closest connection between these two concentrations below or above the adsorption isotherm, without crossing the adsorption isotherm curve on both sides of the adsorption isotherm, respectively. From the shape of these operational lines, information will be obtained about the shape of the elution profiles. The front of the elution profile is described from the operational line connecting C_0 to C_{inj} below the adsorption isotherm curve. The rear will be described from the operational line connecting C_{inj} to C_0 above the adsorption isotherm curve.

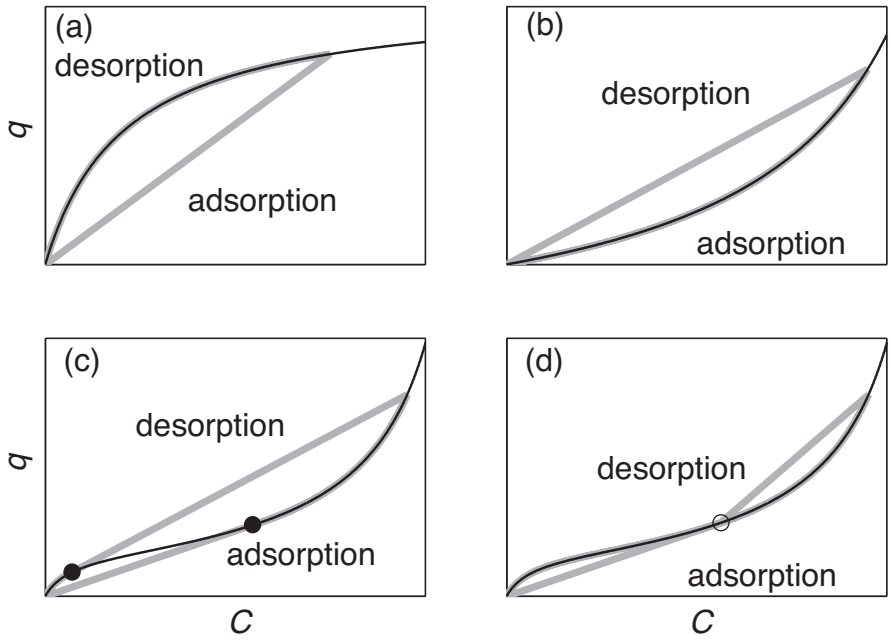

Fig. 1. Different adsorption isotherms (black lines) with corresponding operational lines (grey lines). The adsorption process is the operational line plotted below the adsorption isotherm and the desorption process corresponds to the line located above. (a) Type I adsorption isotherm, (b) type III adsorption isotherm, (c) type II adsorption isotherm from $C = 0$ to high concentration, the filled circles represent adsorption isotherm data not possible to measure. (d) Type II adsorption isotherm: $C_0 = 0$ and C_{inj} = inflection point concentration (circle) followed by a second step where C_0 = inflection point concentration and C_{inj} = high concentration.

In Fig. 1a, a type I adsorption isotherm is plotted (black line), in Fig. 1b a type III adsorption isotherm is plotted (black line) and in Fig. 1c and d adsorption isotherms containing inflection points are plotted (type II). The grey lines are operational lines, which are given by the closest connection between the initial concentration (C_0) and the concentration at the established concentration plateau (C_{inj}, this is identical to the injected concentration). The first case, is the type I adsorption isotherm (*cf.* Fig. 1a). The operational line for the adsorption process is the adsorption isotherm chord resulting in a shock in the front of the elution profile and the desorption process is above the isotherm thus following the adsorption isotherm, resulting in a diffuse rear of the profile. In Fig. 1b on the other hand, a type III adsorption isotherm is presented. Here, the operational line follows the adsorption isotherm for the adsorption process and now the chord instead represents the desorption process, leading to a diffuse front and a shock in the rear of the elution zone.

The same argument holds for adsorption isotherm containing inflection points. In Fig. 1c, the operational lines for a type II adsorption isotherm are depicted for a large injection. When done so in a type II case, it results in operational lines containing cords and parts that follow the adsorption isotherm for both the adsorption and desorption processes. In this case the front contain a shock at low concentration followed by a diffuse part and the rear part of the elution profile will at high concentrations be a shock and ending in a diffuse part at low concentration. The adsorption isotherm part between the filled circles will not be represented in any diffuse part on the elution profile and could therefore not be determined with this experiment. To be able to measure the entire adsorption isotherm it is required two experiments. The first experiment is a large injection where C_{inj} is equal to the concentration of the inflection point (open circle in Fig. 1d). The second experiment has an established feed concentration of the former experiment and an injection with the desired concentration above the feed concentration. This will result in the first part being a type I adsorption isotherm and the second part being a type III adsorption isotherm; both these parts could be determined using Eqs. (4a) and (4b).

3. Applications

In this part, the principles outlined in Section 2 for the determination of adsorption isotherm for types II, III and V adsorption isotherms, will be validated. All chromatograms are calculated using the equilibrium-Dispersive model solved by the orthogonal collocation on finite elements method (OCFE) [26,27]. In all simulations the following settings has been used: 10,000 theoretical plates, total porosity 0.60, length of column is 15 cm, diameter of column 0.46 cm and volumetric flow 1.0 mL/min.

3.1. Type III

The acquisition of adsorption data from a type III system is most straightforward. Similar to the type I adsorption isotherm the data could be determined using the classical integration method of ECP or the slope-ECP method [21], because the adsorption isotherm does not contain any inflection points. Adsorption models, describing type III adsorption isotherms are anti-Langmuir model, this could be modeled by using a Langmuir model with negative association equilibrium constant [28] or the BET adsorption isotherm [29]. The BET adsorption isotherm model could be written as [30]:

$$q = q_s \frac{b_s C}{(1 - b_L C)(1 - b_L C + b_s C)}, \quad (5)$$

q_s is the monolayer saturation capacity, b_s and b_L is the equilibrium constant on the bare surface and on a layer of already-adsorbed solute, respectively. If the solute–solute interactions are strong the adsorption isotherm could become strictly convex downwards (type III), this take place if $b_L \geq b_s/2$, if this does not hold the BET turns to a type II adsorption isotherm [5].

In Fig. 2, a 5 mL of a 10 g/L solution is injected. The true adsorption isotherm is a BET type III, with $q_s = 50$ g/L, $b_s = 0.06$ L/g, and $b_L = 0.04$ L/g. The thin black lines are the corresponding perturbation peaks, the circles are the retention times of the perturbation peaks apex. As discussed in Section 2, the retention time of a perturbation peak is proportional to the slope of the adsorption

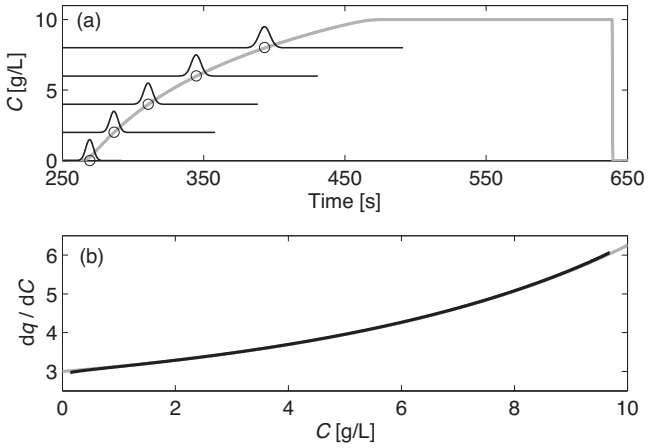

Fig. 2. (a) Elution profile for a type III adsorption isotherm (grey line), the black lines are overlaid perturbation peaks for different concentration plateaus corresponding to the diffuse front. The open circles are the distinct perturbation retention times. (b) True (grey line) and estimated (black line) slope of the adsorption isotherm.

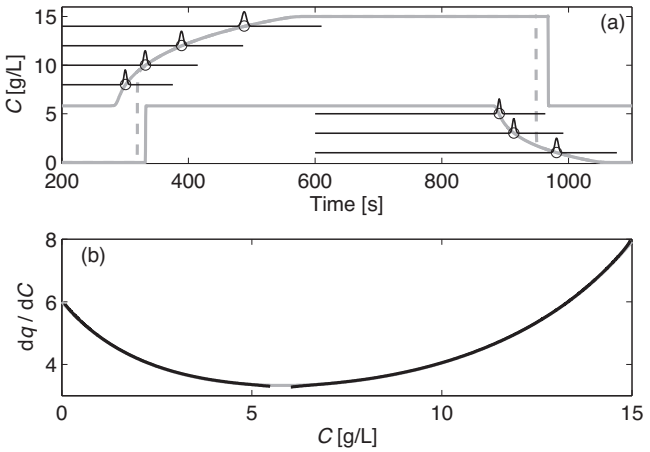

Fig. 4. (a) Elution profile for a type II adsorption isotherm (grey lines). The profile originates from a 10 mL injection of 5.8 g/L and a 15 g/L on a concentration plateau of 5.8 g/L. The dashed line is the elution profile of a 10 mL 15 g/L injection. Overlaid perturbation peaks for different concentration plateaus are plotted (black line). The circles are the perturbation peak retention times. (b) The figure shows the true (grey line) and estimated (black line) slope of the adsorption isotherm, respectively.

isotherm. Here the perturbation peaks have a combined elution with the corresponding concentrations on the diffuse front of the overloaded band profile which clearly demonstrates the usefulness of the slope-ECP method for determination of adsorption isotherms of a type III adsorption isotherm. In Fig. 2b, the determined slope of the adsorption isotherm is plotted as a black line and the true data is plotted as a grey line. From the figure it is clear that the data is excellently predicted and that only small deviations are noted at low and high concentrations where the effect of limited efficiency is most pronounced.

The ECP assumes rectangular injection profiles and contains therefore an inherent very important source of error; the effects of the post-loop dispersion. However, a new injection-technique eliminating this error was recently introduced [19]. Only the case with type I adsorption isotherms was considered. Therefore, it is necessary to investigate if this important source of error must also be eliminated in the case of a type III adsorption isotherm. For this purpose, we numerically calculate overloaded elution zones based on type III adsorption. Injection profiles from a 5 mL rectangular injection and one with a numerical calculated injection profile using a 2D-convection diffusion equation in cylindrical coordinates [20] were compared, see Fig. 3a. The calculated injection profiles were done assuming solutes diffusion coefficient in the eluent of 8.9×10^{-9} m^2/s, straight capillary with inner diameter of 1 mm and flow rate of 1 mL/min using COMSOL multiphysics version 3.5a (COMSOL, Stockholm, Sweden) [20]. In Fig. 3b, overloaded elution profiles for 5 mL injection with rectangular and "experimental" injections are plotted. The fronts of the two profiles have a completely combined elution and are thus unaffected by the injection profile, due to the fact that the front of the elution zone is primarily affected by the first parts of the injection profile and not the dispersed rear part. This is a consequence of the reason why the term for the injection volume is excluded in the corresponding relation for the retention volumes of the front concentrations (see Eq. (2)). Thus, there is no need to use CUT-injections to generate accurate ECP adsorption data for type III adsorption isotherms as long as the elution zone reaches a concentration plateau.

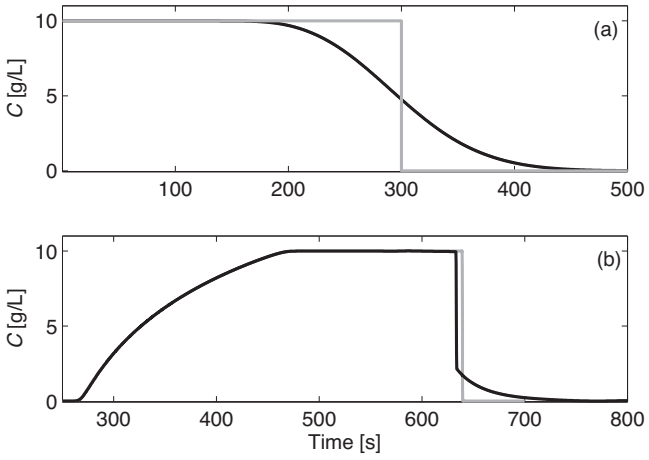

Fig. 3. (a) 5 mL calculated (black line) and rectangular (grey line) injection profile. (b) Elution profiles for a type III adsorption isotherm using calculated injection profiles (black line) and rectangular injection profile (grey line) as boundary condition.

3.2. Type II

Adsorption isotherm that could be used to describe a type II adsorption isotherm is the BET adsorption isotherm, see Eq. (5). However, in this case $b_L < b_s/2$.

Fig. 4a shows overloaded profiles, for a 10 mL injection of 5.8 g/L (grey line) and 10 mL injection of a 15 g/L injection (dashed line) and a 15 g/L on an already established concentration plateau of 5.8 g/L (grey line). The adsorption isotherm parameters are $q_s = 30$ g/L, $b_s = 0.1$ L/g, and $b_L = 0.04$ L/g. The thin black lines are corresponding perturbation peaks and the circles the retention times of the perturbation peaks apex. The reason why it is necessary to inject on a concentration plateau is to eliminate the risk of missing some adsorption data, as discussed in Section 2.1. The initial part of the type II adsorption isotherm is convex upwards resulting in an initial diffuse rear. To be able to determine as much data as possible from this part, a large injection is necessary, with approximately the concentration of the inflection point (C_{Inf}). If the concentration exceeds C_{Inf} adsorption data will be lost, because the shock will start at a lower concentration (see Section 2.1). As the concentration increase, the adsorption isotherm shifts to convex downwards; this is why the front is diffuse at high concentrations (see Fig. 4a). Thus, the simplest way to include also the high concentration adsorption data is to make an injection on an already established concentration plateau with concentration C_{Inf}. However, this exact concentration level is experimentally hard to find, before the isotherm is

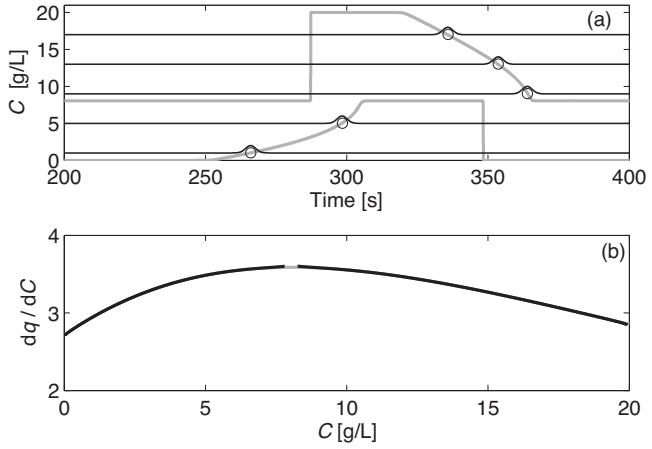

Fig. 5. (a) Elution profiles for a type V adsorption isotherm. The profiles originate from a 1 mL injection of 8.04 g/L and a 20 g/L injection on a concentration plateau of 8.04 g/L (grey lines). Overlaid perturbation peaks for different concentration plateaus are plotted (black line). The circles are the perturbation retention times. (b) True (grey line) and estimated (black line) slope of the adsorption isotherm.

known. Therefore, we propose as a rule of thumbs, that the low concentration injection should have the concentration of equal or less than C_{Inf} and the concentration plateau should be larger or equal to C_{Inf}. The larger the difference is between the selected concentrations and C_{Inf}, the more amount of adsorption data will be lost.

In Fig. 4b, the slopes of the predicted adsorption isotherm (black line) and the true adsorption model (grey line) are overlaid. As can be seen, a narrow window of data is missing around the adsorption isotherm inflection point, due to the limited efficiency in the separation system. However, if these data points are of outmost importance, additional perturbation peaks at this concentration could be made to complement the ECP data.

3.3. Type V

Type V adsorption isotherm is a type III adsorption isotherm that reaches a saturation capacity at high concentrations. One model describing this is the Moreau model [5]:

$$q = q_{\mathrm{s}} \frac{KC + IK^2C^2}{1 + 2KC + IK^2C^2}, \tag{6}$$

where K is the association equilibrium constant and I is the solute–solute interaction term. The Moreau model has successfully been used to adsorption of propranolol to ODS columns [31] describe charged solute adsorption to interactions.

In Fig. 5a, elution profiles are plotted for 1.0 mL injection of 8.04 (grey line) and 20 g/L (grey line) on an already established concentration plateau of 8.04 g/L. The elution zones are described with a Moreau model with: $q_{\mathrm{s}} = 178.8$ g/L, $K = 0.0152$ L/g, and $I = 5$). The thin black lines are corresponding perturbation peaks and the circles the retention times of the perturbation peaks apex. In Fig. 5b, the corresponding determined adsorption isotherm is plotted.

As can be seen in Fig. 5a the adsorption isotherm will start with a diffuse part. This data is collected with the 8.04 g/L injection (grey line). At higher concentration the diffuse part will be situated at the rear of the profile. The high concentration data is determined with the second injection of 20 g/L at an already established concentration plateau of 8.04 g/L (grey line).

If now the determined slope of the adsorption isotherm data in Fig. 5b is inspected, it can be seen that the data is excellently predicted. Some adsorption data is missing around the adsorption isotherm inflection point in this case also, due to limited efficiency of the separation system.

So far only systems with one inflection point have been discussed. If the adsorption process is described with adsorption isotherms containing more inflection points an extra injection is required for each inflection point. For example a system containing two inflection points would require three injections. The first injection is then done with a concentration up to the first inflection point. The second injection is done with a concentration up to the second inflection point on a concentration plateau of the first inflection point. Finally, the third injection is done up to the desired concentration of the adsorption isotherm determination on a concentration plateau of the second inflection point. Theoretically this would work perfectly. However, as has demonstrated above, some adsorption data is not possible to determine around the inflection points due to the limit efficiency of the separation system. This "loss" will increase with decreasing efficiency of the separation system. If we try to determine very complicated adsorption isotherms several patches without data will appear. On the other hand, such extreme adsorption isotherms are very unusual.

4. Conclusions

The elution by characteristic point (ECP) method is a rapid chromatographic method for determination of adsorption isotherms. But, it has suffered from two important drawbacks as compared to the much more laborious frontal analysis (FA) method; a less degree of accuracy and limitations to only simple type I adsorption isotherms (*e.g.* Langmuir or similar). However, recent improvements have been made on the accuracy of the method (see below, cut-injections) [19]. In this paper it is demonstrated and validated how the method can be expanded to generate adsorption isotherm for other than type I. All together, these improvements will probably turn the ECP method to be the prime candidate, together with the classical but more tedious FA method, for chromatographic generation of adsorption isotherms. One remaining limitation is that only systems with at least moderate high column efficiencies could be studied if very accurate adsorption isotherms are required. General guidelines of the minimum efficiency required is hard to obtain because it depends on the actual system, such studies have so far only been conducted for the Langmuir [16] and bi-Langmuir models [17], respectively.

Adsorption isotherms were successfully determined with the ECP method for a type III (concave upwards), a type II and a type V adsorption isotherm. We limited our investigation to adsorption isotherm containing only one inflection point (types II and V). However, as discussed above, additional injections on a plateau is required for each additional inflection point.

Determinations of adsorption isotherm containing inflection points were possible due to two modifications. First, the retention volume was not integrated instead, raw slope data was used. Using raw slope data does not require that the diffuse part of the profile is continuous; this is a very recent ECP method improvement [21]. Secondly, two separate injections were made. The first injection was up to the adsorption isotherms infection point concentration. The second injection was to the desired concentration but now on an already established concentration plateau of the former injection concentration.

Previously, we have demonstrated how the accuracy of the ECP method could be increased considerably by experimentally generating rectangular injection profiles [19]; we called these cut-injections [19] and they were recommended for general ECP work. In this actual study, we could demonstrate convincingly that CUT-injections are not necessary for type III adsorption isotherms

as long as the elution zone reaches a concentration plateau (*cf.* Fig. 3b).

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