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Evaluation of sugar sorption isotherm measurement by frontal analysis under industrial processing conditions

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Abstract

This paper evaluates frontal analysis for routine sugar isotherm measurements at industrial conditions, that is concentrations up to 400 kg/m^3 and a temperature of 60 °C. Sugar isotherms for a gel type cation-exchange resin loaded with metal ions were measured in a HPLC set-up equipped with a UV detector. It is shown experimentally that isotherms obtained with large concentration steps (step series method) underestimated the isotherm. The underestimation is larger for larger resin particle size. In contrast, isotherms obtained with small concentration steps (staircase method) yielded correct isotherms. The seldom-mentioned change of the sorbent volume during the course of an isotherm measurement is discussed. It is shown that shrinking of 4% cross-linked resin at high sugar concentration has a negligible effect on the isotherm. Furthermore, the isotherms obtained with staircase frontal analysis agreed very well with those obtained with the independent, though more laborious and time-consuming, adsorption–desorption method. Staircase frontal analysis is shown to be convenient and accurate and is therefore recommended for isotherm measurements covering large concentration ranges.

Keywords: Frontal analysis; Isotherms; Sorption; Cation-exchange resin; Sugars

1. Introduction

Isotherms represent important information to understand the interaction between a solute and an adsorbent. Also, isotherms supply valuable information for the selection of a suitable adsorbent for a given separation problem. They are required for the design of chromatographic separation processes [1,2]. Unfortunately, it is in general not possible to predict isotherms. Instead, isotherms are determined experimentally. It was shown [3–5] that small deviations in the applied isotherms resulted in substantial differences of the calculated chromatographic column concentration profiles. Thus, it is important to measure the isotherm accurately.

A multitude of isotherm measurement methods was developed. They are reviewed in detail elsewhere [6–8]. Isotherm methods can be divided in static and dynamic methods. The most accurate static method is the adsorption–desorption method. However, this method is laborious and time-consuming. Therefore, several dynamic isotherm measurement methods were developed. Frontal analysis is one of the most popular dynamic isotherm measurement methods, because it is fast, accurate and easily automated [6,9]. Unlike several other dynamic methods, it is not limited to HPLC columns, that is columns with several thousand theoretical plates [6,10].

In our research we needed a fast and accurate measurement method for sugar sorption by ion-exchange resins. Typical operating conditions in industrial sugar separation processes are temperatures in excess of 60 °C and sugar concentrations around 500 kg/m^3. Therefore, isotherms should be measured at these conditions. Some authors applied frontal analysis [11–14] for the measurement of sugar isotherms but without comparing their isotherms with the results of other

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methods. Only one publication [15] was found which reports equilibrium sorption of sugars on ion-exchange resins using more than one method, including frontal analysis. The distribution constant varied for glucose from 0.14 up to 0.18 and for fructose from 0.45 up to 0.52 for the same resin and temperature, depending on the method. No explanation was given for the observed differences.

For silica adsorbents good agreement between the dynamic frontal analysis method and the static adsorption–desorption method was reported in several studies with various adsorbates other than sugars at low concentrations [10,16,17]. While most authors assume a constant adsorbent volume and porosity during isotherm measurement, some studies [18,19] found that it considerably varies. For example, the porosity of silica was found to decrease with increasing adsorbate concentration due to increasing volume of the adsorption layer [18]. Another example [19] showed that the C_{18} layer on silica expanded with increasing methanol concentration in the aqueous eluent, thereby decreasing the volume available to the mobile phase. It is crucial to know the adsorbent volume and porosity exactly to be able to calculate the isotherm accurately with dynamic methods. However, the cited references on silica type adsorbents present results measured at low temperatures or at low concentration, whereas sugar separation processes are performed at high concentrations and temperatures. Moreover, we use ion-exchange resins instead of silica.

The most abundantly studied adsorbents for sugar sorption are sulfonated poly(styrene-*co*-divinylbenzene) ion exchange resins in Ca^{2+} form. This resin is applied in the industrial-scale chromatographic separation of glucose and fructose. Table 1 shows distribution constants reported in literature for this type of resin. The degree of cross-linking of the resin has a substantial influence on the amount of sugar sorption [20–22]. To facilitate comparison, the data in Table 1 are therefore grouped by degree of cross-linking. In addition conditions such as temperature, concentration and degree of Ca^{2+} loading may vary from reference to reference. From Table 1, it is observed that even for the same resin type, the reported distribution constants show significant differences. For example, the sorption of fructose on Lewatit MDS 1368 resin differs up to almost a factor 2 at equal temperature (compare numbers 9 and 10). In addition, most authors assumed constant resin volume and a linear isotherm a priori. Furthermore, details about resin pre-treatment and measurement procedure were not reported. Therefore, these data are unusable as a reference for evaluation of an isotherm measurement procedure.

The goal of this work was to evaluate frontal analysis and its suitability for routine sugar isotherm measurements on gel type cation-exchange resins loaded with various metal ions under industrial processing conditions. To our knowledge there is no standardized reference system available for the measurement of liquid phase sorption isotherms. Therefore, frontal analysis was studied by quantifying the repeatability and the inter-column precision of the isotherms.

Table 1
Comparison of single component glucose and fructose distribution constants (defined by Eq. (9)) for Ca^{2+} loaded PS-DVB resins, the separation factor $\alpha = (K_{fructose})/(K_{glucose})$

No.	Sorbent	DVB (%)	T (°C)	Method	$K_{glucose}$	$K_{fructose}$	Maximum concentration	α	Reference
1	Dowex 50W-X8	8	Not reported	Pulse	Not reported	0.57–0.66	30 kg/m^3	–	[38]
2	Dowex 50W-X8	8	25	Pulse and frontal analysis	α-Glucose: 0.228, β-glucose: 0.294	β-Fructose: 0.657	100 kg/m^3	2.2–2.9	[12]
3	Dowex 50W-X8	8	25	Pulse	0.25	0.59	Not reported	2.4	[39]
4	Dowex 50W-X8	8	30	Pulse	0.30	0.80	Not reported	2.7	[40]
5	Dowex Monosphere 99	6	30	Various	0.14–0.19	0.45–0.52	30 kg/m^3	2.8	[15]
6	Dowex Monosphere 99	6	55	Column adsorption-desorption	0.17	0.43	Not reported	2.5	[41]
7	Dowex Monosphere 99	6	70	Pulse	$0.25 + 5.1 \times 10^{-2} c_{glucose}$	$0.47 + 7.0 \times 10^{-2} c_{fructose}$	600 g/kg	1.3–1.9	[5]
8	Lewatit MDS 1368	Not reported	40	Pulse	0.19	0.32	Not reported	1.7	[42]
9	Lewatit MDS 1368	Not reported	40	Static adsorption	0.24	0.32	350 kg/m^3	1.3	[42]
10	Lewatit MDS 1368	Not reported	40	Frontal analysis	0.32	0.61	Glucose 300 kg/m^3 Fructose 500 kg/m^3	1.9	[43]
11	Lewatit MDS 1368	Not reported	60	Frontal analysis	0.32	0.54	Glucose 300 kg/m^3 Fructose 500 kg/m^3	1.9	[43]
12	Duolite C204	Not reported	52.5	Pulse	0.50	0.75	Not reported	1.5	[44]
13	Duolite C204	Not reported	55	Pulse	0.36	0.46	Not reported	1.3	[4]
14	Duolite C204	Not reported	70	Pulse	0.50	0.67	Not reported	1.3	[44]

In addition, the seldom-mentioned sorbent shrinking during isotherm measurement is discussed and measured as a function of glucose concentration. Also, the staircase and step series method are compared including the effect of the size of the concentration steps. Finally, a comparison is made between frontal analysis and the adsorption–desorption method.

2. Materials and methods

2.1. Chemicals

The poly(styrene-*co*-divinylbenzene) (PS-DVB) sulfonated cation exchange resins, Dowex 50WX4-400, mesh size 200–400, and Dowex 50WX4-100, mesh size 50–100 (both from Aldrich, Steinheim, Germany), were purchased in H^+ form, were 4% cross-linked and had a bead diameter of 38–74 μm (throughout this paper named 'fine' resin) and 150–297 μm ('coarse' resin), respectively. After washing with deionised water and elutriation of fines, the resin was converted to the Na^+ form by titrating 1.00 M NaOH to a resin suspension in pure water. Addition of alkaline solution was stopped when the pH increased sharply to 9. To ensure maximum but not necessarily complete loading with Na^+ further ion exchange was performed in a column with 0.200N NaCl. All water used was prepared with a MilliQ apparatus (Millipore, Bedford, MA, USA). The dry substance content of the resin was determined by drying until constant weight in an oven at 105 °C. D-Sucrose, D-glucose and D-galactose (Aldrich), and D-fructose and lactose monohydrate (Merck, Darmstadt, Germany) were used for isotherm measurements.

2.2. Column set-up

The data were acquired on a Knauer HPLC set-up (Berlin, Germany), which comprised a K-1500 Solvent Organizer, a K-5020 degasser, a K-1001 pump, a dynamic mixing chamber, and an electronic six port/three way valve. A UV spectrophotometer (WellChrom K-2600) was used for the monitoring of column effluents under the applied industrially representative conditions (sugar concentration up to 400 kg/m^3 and 60 °C). The detector acquired data at 190 nm, the lowest wavelength at which the detector is able to operate and therefore as close as possible to 188 nm, the wavelength at which sugars exhibit a maximum in light absorption [23].

The column, Superformance 300-16 (Götec, Muehltal, Germany) had a maximum length of 0.300 m and an internal diameter of 15.95 mm. It was equipped with a water jacket connected to a circulating water bath at 60 ± 0.01 °C. The extra-column volume V_{ext} was 0.95 ± 0.15 cm^3.

2.3. Void volume and sorbent volume

The sorbent volume and the interparticle bed porosity were determined with high molecular weight (2.0×10^3 kg/mol) dextran T2000 (Amersham Pharmacia, Uppsala, Sweden),

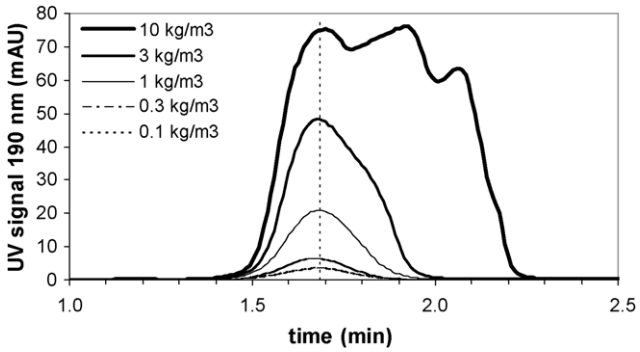

Fig. 1. Effect of dextran concentration on the eluted peak, fine (200–400 mesh) 4% cross-linked Na^+ loaded resin, injection volume 1.00 cm^3, flow rate 10.0 cm^3/min, 60 °C.

hereafter named dextran. It was assumed that the dextran molecules cannot penetrate the gel type resin interior due to size exclusion [24]. The exclusion limit is of the order of magnitude 1 kg/mol. From the retention time t_R of dextran pulses (1.00 cm^3) [25] the interparticle bed porosity ε_b was calculated from:

$$\varepsilon_b = \frac{V_o}{V_c} = \frac{\phi t_R - V_{ext}}{V_c}, \quad (1)$$

where V_o is the liquid hold-up of the bed, V_c the internal volume of the empty column and ϕ is the flow rate. Although several authors [5,11,26–30] used dextran to measure interparticle porosity of columns packed with gel type ion-exchange resins, none of them reported on the dextran concentration they applied. To investigate the effect of dextran concentration Fig. 1 shows chromatograms of dextran pulses on 4% cross-linked Na^+ loaded resin and eluted with water at 10 cm^3/min. The results show that at high dextran concentration, viscous fingering [6] influences the shape of the dextran peak. Furthermore, at concentrations of 1.0 kg/m^3 or lower the retention time is independent of concentration and 1.0 kg/m^3 is therefore a suitable concentration for determination of the liquid volume in the column. Using this concentration, the repeatability of the resin volume was within ±1%.

The fully swollen resin volume V_S^0 was calculated from:

$$V_S^0 = V_c - V_0 = (1 - \varepsilon_b)V_c, \quad (2)$$

To quantify resin shrinking as a function of glucose concentration the retention time of dextran pulses at different glucose concentration plateaus was measured at 250 nm (at 190 nm the dextran could not be observed due to the strong glucose signal).

2.4. Frontal analysis

With frontal analysis isotherms are determined from the breakthrough times of step changes in the feed concentration. The principle of frontal analysis is shown schematically in Fig. 2. Two types of commonly applied feed concentration

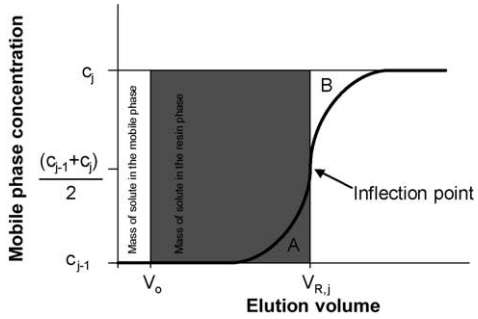

Fig. 2. Schematic breakthrough curve typical for frontal analysis and showing the principle of calculation of the amount of solute in the resin, indicated by the hatched area. The thick solid line represents the solute concentration in the mobile phase at the column outlet. The elution volume $V_{R,j}$ is obtained from either the inflection point of the curve, the half height $(C_{j-1} + C_j)/2$ or from equaling area A to B (integration method, see also Eq. (5)).

profiles in frontal analysis, the staircase method and the step series method [31], shown schematically in Fig. 3, were applied. In the staircase method, the feed concentration is stepwise increased, whereas in the step series method the column is equilibrated with pure desorbent in between successive concentration steps. For the staircase method, the change in sorbent loading due to a step in the feed concentration was calculated from:

$$q_j = q_{j-1} + \frac{(c_j - c_{j-1})(\phi(t_{R,j} - t_{0,j}) - (V_0 + V_{ext}))}{{V_S}^0},$$

$$\text{with } j = 1, 2, \ldots, 10, \tag{3}$$

where q_j is the mass of the sugar sorbed by the column packing after the jth step per unit resin volume V_S^0 in equilibrium with the concentration c_j, $t_{R,j}$ the breakthrough time of the jth step and $t_{0,j}$ is the start time of the concentration step.

In the step series method, the column initially contains no solute, but is flushed with pure water and a step injection of a solution of concentration c_j is applied at the inlet of the column. Before the next step is supplied to the column, the column is flushed again with 200 cm^3 pure water, which amounts up to 10 times the column void volume. The adsorbent loading for the step series method was obtained with $q_{j-1} = 0\ kg/m^3$ and $c_{j-1} = 0\ kg/m^3$. Therefore, Eq. (3) can be simplified to:

$$q_j = \frac{c_j(\phi(t_{R,j} - t_{0,j}) - (V_0 + V_{ext}))}{V_S^0}$$

$$\text{with } j = 1, 2, \ldots, 10. \tag{4}$$

The breakthrough time $t_{R,j}$ was determined with three methods: (1) integration, (2) inflection point, and (3) half height method [31]. In the integration method, $t_{R,j}$ was calculated from the definition of the breakthrough time, which corresponds to equalling area A to B in Fig. 2:

$$t_{R,j} = \frac{\int_{t_{0,j}}^{t_{e,j}} (c_j - c)\,dt}{c_j - c_{j-1}}, \tag{5}$$

where $t_{0,j}$ and $t_{e,j}$ are the start time and end time of step j, respectively, c is the concentration of sugar at the column outlet. The inflection point was obtained from the calculation of the first derivative of the detector signal. The integration method is theoretically the best method, since it follows the definition of the breakthrough time given by Eq. (4). However, for convenience the breakthrough time may preferentially be determined by the inflection point method or half height method [31]. The two approximate methods are only applicable for sharp symmetrical S-shaped breakthrough fronts of the error function type because in that case the breakthrough is exactly equal for all three methods. Sufficiently low flow rates were chosen to ensure sharp fronts, which was 10 cm^3/min for fine resin and 1 cm^3/min for coarse resin, resulting in a measurement time of 2 and 20 h, respectively, for an isotherm of 10 datapoints. Consequently, there was no significant difference between the isotherms determined with the three methods for breakthrough determination with staircase frontal analysis under the applied conditions.

For the isotherm data point calculations it is necessary to know exactly the applied flow rate and the solute concentration. Collecting and weighing the column effluent calibrated the flow rate of the pump. The column set-up delivered concentrations with a relative accuracy of 1.5%, which is sufficient for isotherm measurements. During an isotherm measurement run, the electronic valve was used to switch the flow from the column to a bypass or vice versa allowing a new con-

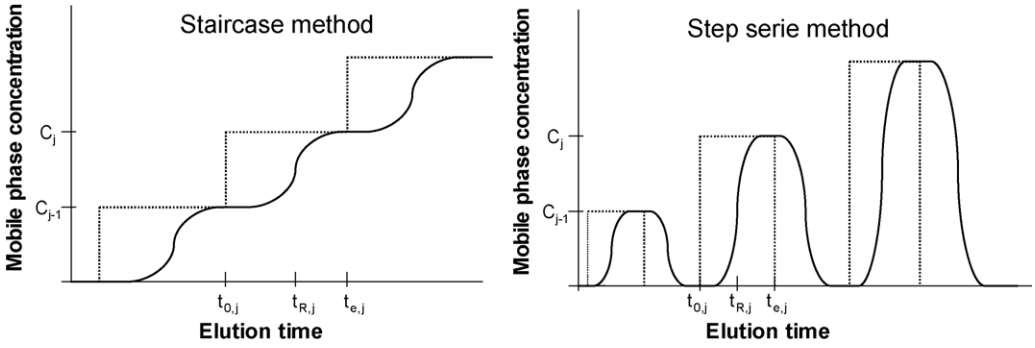

Fig. 3. Schematic diagrams showing the column feed concentration (dashed line) and the effluent concentration (solid line) for frontal analysis isotherm measurement with the staircase and the step series method.

centration level to establish in the tubing before switching to the column.

2.5. Adsorption–desorption method

The adsorption–desorption method experiments were performed in two ways. In the first method, batch adsorption–desorption [7,32], the isotherms were determined by contacting overnight filtrated (filter type 5971/2, Schleicher & Schuell, Dassel, Germany), weighted resin samples of about 5 g with different sugar solutions (25 cm^3) of known concentration c^0 in screw capped, sealed Erlenmeyers and placing them in a shaking water bath at 60 °C. Subsequently, the resin was separated from the sugar solution on a sintered glass filter (Duran number 3, Schott, Mainz, Germany). This procedure was repeated three times to ensure equilibrium between resin and the sugar solution with concentration c^0. The sugar concentration in the filtrate was checked by measuring the density with an Anton Paar (Graz, Austria) DMA 58 density meter. The standard error of the concentration measurement was <0.020 kg/m^3. Subsequently, the filtrated sugar loaded resin was suspended in 50 cm^3 water to desorb the sugar overnight. This step was repeated once to ensure >99% desorption of the sorbed sugar. The sugar concentration in the combined desorption liquids was determined by measuring the density. The isotherm data were calculated using:

$$Q = \frac{(m_{\mathrm{des}}/\rho_{\mathrm{des}})c_{\mathrm{des}}}{W_{\mathrm{S}}}, \tag{6}$$

where Q is the sugar mass per mass unit of resin in equilibrium with a solution of concentration c^0, m_{des} the total mass of the combined desorption liquid, ρ_{des} the density of the eluent, c_{des} the concentration of the sugar in the desorption liquid and W_S is the dry mass of the resin.

In the second method, column adsorption–desorption [7,15], the column was fed with a solution of known concentration after equilibration with pure water. After breakthrough the flow of the solution through the column was continued until the detector signal was constant to ensure equilibrium between feed solution and resin. Then, the column was disconnected from the chromatographic set-up and closed to prevent bleeding. The chromatographic system was flushed with water to remove extra-column sugar. Subsequently, the column was eluted with water to desorp the sugar. The column effluent was collected until the detector signal indicated that pure water eluted from the column. The sugar concentration in the desorption liquid c_{des} was determined from the density of the collected liquid. V_{des} was calculated from the product of density and the mass of the collected liquid. Sorption isotherm data were calculated with:

$$q = \frac{(m_{\mathrm{des}}/\rho_{\mathrm{des}})c_{\mathrm{des}} - (V_0 + V_{\mathrm{ext}})c^0}{V_S^0}, \tag{7}$$

where q is the mass of sugar per unit volume of resin in equilibrium with the feed concentration of the column c^0. The liquid hold-up V_0 was corrected with the extra-column volume, in this case only the volume of the in- and outlet of the column, which was 0.55 ± 0.15 cm^3.

2.6. Isotherm data processing

The measured isotherms appeared to be linear or slightly concave and were fitted with an equation, which was used previously [33] to describe a concentration dependent sugar distribution constant K:

$$q = a\,c^2 + b\,c, \tag{8}$$

and,

$$K \equiv \frac{q}{c} = a\,c + b \tag{9}$$

where q [kg/m^3] is the mass of sugar per unit volume of resin in equilibrium with the liquid concentration c [kg/m^3], a [m^3/kg] is an equilibrium parameter correcting for the concentration dependence of the distribution constant at higher sugar concentrations and b the apparent Henry's law constant, the slope of the isotherm at infinite dilution. Isotherm data from column methods were expressed per unit volume resin, whereas the batch adsorption–desorption method yields sorption per unit mass of dry resin. The equilibrium parameter $a > 0$ m^3/kg for concave isotherms. If the sorption calculated from the non-linear fitted correlation differed less than 2% from the linear fitted correlation, then the linear correlation was used ($a = 0$ m^3/kg). To compare results from column and waterbath measurements, the former data were recalculated by replacing the resin volume V_S^0 in Eq. (3) with the mass W_S of dry resin.

3. Results and discussion

3.1. Frontal analysis

3.1.1. Repeatability and inter-column precision

The glucose isotherms for a triplo frontal analysis isotherm measurement with fine, 4% cross-linked resin measured at a flow rate of 10 cm^3/min at 60 °C indicated that the repeatability of the isotherms was within ±2%. The inter-column precision of the frontal analysis isotherm measurements was determined by preparing two columns with fine resin. The isotherms of several sugars on these columns, measured at 10 cm^3/min were in excellent agreement with isotherms from duplicate columns. These results indicated that the inter-column precision of the isotherm was within ±3% under the described conditions. With silica columns other authors obtained similar isotherm measurement repeatability and inter-column precision with frontal analysis [34].

3.1.2. Influence of resin shrinking on isotherm

The specific volume of gel type ion-exchange resins is a function of resin properties, solvent type, solute concen-

tration and temperature [35]. During the isotherm measurement the solute concentration increases strongly and the resin shrinks, due to increased osmotic pressure of the solution and thereby increasing the void volume V_0 in Eqs. (3), (4), and (7). Resin shrinking is usually not quantified under relevant conditions, if at all. Therefore, many authors [4,5,11,14,15,32] conveniently assumed that the resin did not shrink and implicitly assumed that the void volume was also constant. In case of frontal analysis this implicates that V_0 in the nominator of Eq. (3) is supposed to be constant. To investigate this the following equation was fitted to the experimentally obtained volume of fine 4% cross-linked Na^+ loaded resin:

$$V_a = V_a^0(1 - 7.0 \times 10^{-5} c_{glucose}) \quad (10)$$

The results were in close agreement with data from literature [32]. To check the validity of the assumption that V_0 is constant, the glucose isotherm on fine, Na^+ loaded resin was calculated under the assumption of no shrinking, thus both V_S and V_0 are constant and equal to the value in pure water. This isotherm was compared with the isotherm of a shrinking resin with a volume V_S given by Eq. (10) and a void volume V_0 equal to $V_c - V_S$ in Fig. 4 (the two upper isotherms). It is assumed that shrinking is instantaneous and over the complete volume of the column. However, during breakthrough of a concentration front the column is in a transient state and the resin may be shrinking. Our approach is therefore a rough estimate only and represents the worst case, which is maximum error in the isotherm. It is shown in Fig. 3 that the isotherm with constant resin volume is slightly overestimated up to 1.4%. From Eq. (3) it can be seen that shrinking affects the calculated amount of sorbed sugars q_j in two ways; q_j increases due to the use of V_S instead of V_S^0 and q_j decreases due to the use of the actual void volume V_0 instead of the void volume in pure water. Thus, the effects partly compensated each other. The overestimation of q_j is so small that shrinking was neglected in further isotherm data calculations. Throughout further work the resin volume in water, V_S^0 and a constant liquid hold up V_0 for calculation of the isotherm data with Eq. (3) were used. Furthermore, Fig. 3 shows that Eq. (8) fits the experimental data very good. The value of the isotherm parameters was $a = 2.3 \times 10^{-4}$ m^3/kg and $b = 0.41$ for the isotherm. These values hardly differed from the values for the isotherm corrected for shrinking ($a = 2.4 \times 10^{-4}$ m^3/kg and $b = 0.41$).

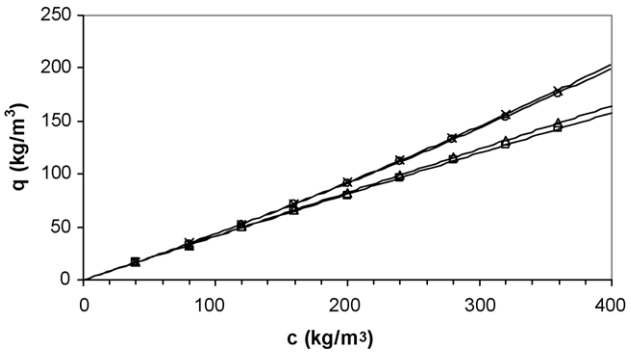

Fig. 4. Glucose isotherms on fine (200–400 mesh), 4% cross-linked, Na^+ loaded resin measured with frontal analysis, flow rate 10.0 cm^3/min, temperature 60 °C. Symbols represent measurements, lines represent best fit of Eq. (8), (×) staircase method constant resin volume assumed, (◯) staircase method concentration dependent resin volume, (△) step series method constant resin volume assumed, (□) step series method concentration dependent resin volume.

Although usually constant adsorbent volume is assumed it is certainly not always a valid assumption. For systems exhibiting very low sorption a small error in V_0, for example, due to shrinking of the sorbent strongly influences the factor $\phi t_{R,j} - V_0$ and hence the calculated value of q_j in Eq. (3). It is therefore recommended to measure the porosity as a function of solute concentration.

3.1.3. Staircase versus step series method

As described above both the staircase method and the step series method were applied in frontal analysis. Obviously, the step series method has the disadvantage that it takes more time, because the column has to be equilibrated with pure mobile phase in between concentration steps. The glucose isotherms on fine, Na^+ loaded resin, determined with the staircase method and the step series method at 10 cm^3/min are compared in Fig. 3. It is observed that the isotherm obtained with the step series method is lower than the isotherm obtained with the staircase method. The observed difference might have been due to incomplete regeneration between the individual runs during the application of the latter method. This was investigated by doubling the elution time of the desorption interval (desorbent volume up to 200 cm^3 for each step). However, no change in the isotherm was observed and it was still lower than with frontal analysis. This indicates that incomplete desorption is not the cause of the observed differences.

The first concentration step in both methods is equal. Hence, the isotherm points for the lowest concentration on the isotherm agree exactly. However, in the step series method the concentration steps become larger for increasing feed concentration. That it is the adsorption–desorption isotherm that is underestimated, and not the frontal analysis isotherm that is overestimated was confirmed by performing a step series measurement with glucose on coarse, Na^+ loaded resin in which both the adsorption and desorption fronts were used to obtain breakthrough times. For each desorption front the column effluent was colleted and the amount of glucose determined. The glucose isotherm was calculated using Eq. (7). Fig. 5 shows the isotherms obtained at 1.00 cm^3/min. For comparison the isotherm obtained with staircase frontal analysis was included. The isotherm obtained with frontal analysis is in close agreement with the isotherm obtained with the column adsorption–desorption method. In contrast, the isotherm obtained with the step series method is either higher (desorption front) or lower (adsorption front) than the isotherms obtained with the other methods, while it was expected that the adsorption fronts and desorption fronts would deliver the same isotherm. Apparently, the fronts of the step

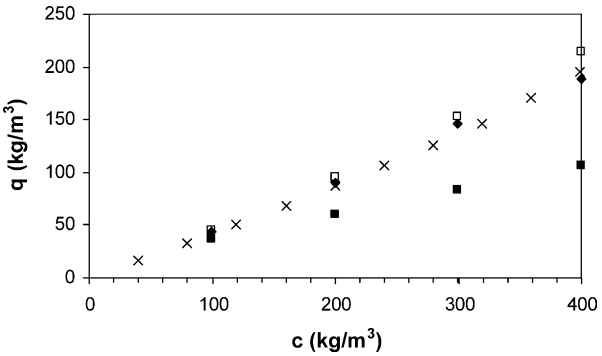

Fig. 5. Comparison of glucose isotherms obtained with different isotherm measurement methods, coarse (50–100 mesh) 4% cross-linked Na^+ loaded resin, flow rate 1.00 cm^3/min, temperature 60 °C, (■) step series frontal analysis adsorption fronts, (□) step series frontal analysis desorption fronts, (♦) column adsorption–desorption method, (×) staircase frontal analysis.

series method are more prone to slow mass transfer than the staircase fronts. Consequently, under these conditions only the integration method is valid for breakthrough volume determination. The error made in the isotherm is smaller using desorption fronts instead of adsorption fronts. This may be due to the self-sharpening effect of desorption fronts, which is characteristic for concave isotherms.

To investigate further the difference between the staircase and step series method, measurements were performed with the step series method at 1 cm^3/min. A four-step isotherm measurement with a maximum glucose concentration of 40 kg/m^3 on the same column yields isotherms identical to those obtained with a four-step staircase method. It is concluded that the staircase and the step series method converge to the same result, when the glucose concentration is decreased.

In the step series method the column is far from equilibrium state for the high concentration measurements, while in the staircase method the column is always close to equilibrium when a sufficient number of steps is chosen. This explains that the step series method is more prone to effects of mass transfer.

The conclusion is that the step series method underestimates the sorption isotherms when high concentrations are applied. These experimental results are in agreement with the conclusion of Sajonz et al. [31] obtained from simulations that changes in the apparent dispersion coefficient during a concentration step cause errors in the determination of the breakthrough volume. Such large changes in the apparent dispersion coefficient might occur when large concentration steps are applied such as in the step series method. Therefore, it is recommended to use of the staircase method instead of the step series method for columns with less than 250 theoretical plates.

A comparison of the two lower isotherms in Fig. 3 obtained with the step series method, with the two upper isotherms obtained with the staircase method shows that the shift, representing the effect of assuming constant resin volume, observed for the step series method is larger (up to 4.1%) than for the staircase method (up to 1.4%). It should be realised that the differences observed in the shift are not caused by differences in the actual shrinking of the resin. Instead, it is merely a consequence of the isotherm calculation method. In the step series method, the assumed resin volume is further away from the true resin volume than in the staircase method.

3.1.4. Comparison of frontal analysis with adsorption–desorption methods

It was shown above that isotherms measured with frontal analysis are precise, i.e. they have low random measurement error. The accuracy, i.e. the absence of systematic experimental error, of the isotherm is discussed here. Both frontal analysis and the column adsorption–desorption method are based on a mass balance. Although the column adsorption–desorption method is more complex and longer than frontal analysis it does not depend on the determination of the breakthrough volume. The column adsorption–desorption method was therefore used to check the results obtained with frontal analysis. In Fig. 6, the glucose isotherm measured with frontal analysis for fine, Na^+ loaded resin at a flow rate of 10 cm^3/min was compared with the isotherm obtained with the batch adsorption–desorption method for the same resin and for coarse Na^+ loaded resin. Any systematic error originating from the use of the column set-up will be verified by measurements with the batch adsorption–desorption method. The batch adsorption-desorption method yields isotherm data per unit mass resin. To facilitate comparison of the two methods, the sorption data from the frontal analysis method were also expressed in gram sugar per gram dry resin. It is observed from Fig. 6 that there is a slight difference between the isotherms obtained with the batch adsorption–desorption method and frontal analysis. Any variation of the error made in the dry substance determination adds to systematic differences observed be-

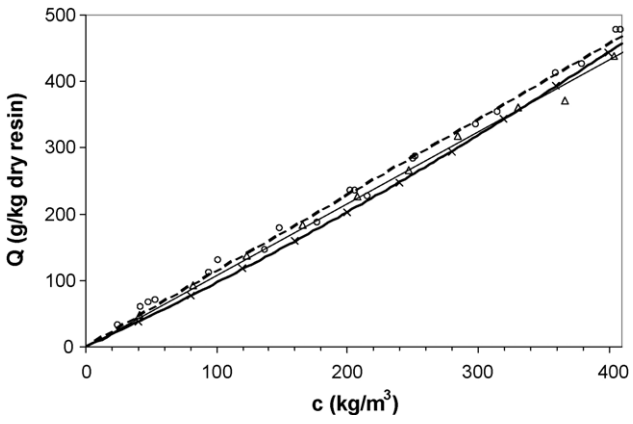

Fig. 6. Comparison of isotherm measurement methods with fine (200–4000 mesh) and coarse (50–100 mesh) 4% cross-linked resin in Na^+ form, flow rate 10.0 cm^3/min, temperature 60 °C, solute glucose. Symbols represent measurements, lines represent best fit of Eq. (8), (◯) and (- - -) batch adsorption–desorption with fine resin, (△) and (—) batch adsorption–desorption with coarse resin, (×) and (▬) frontal analysis with fine resin.

tween isotherms. Furthermore, the isotherm obtained with the batch adsorption–desorption method may be overestimated due to sugar solution adhering to the filtrated resin prior to desorption. Poor phase separation is known to be responsible for unreliable results in ion exchange studies [36]. The adhering sugar ends up in the desorption liquid and is attributed to sorption. A few percent adhering sugar solution has an influence of the order of the difference observed between the isotherm obtained with frontal analysis and the batch adsorption–desorption method. It can be expected that the effect of adhering solution is more severe for fine, low capacity adsorbent than for coarse, high capacity adsorbent. Indeed the isotherm for coarse resin is slightly lower than the resin for fine resin and agrees within experimental error with the isotherm obtained with frontal analysis. Determination of the water content was shown to be impossible by means of a simple heating procedure [37]. The uncertainty about the exact amount of adhering water is a serious disadvantage of the batch adsorption–desorption method.

Furthermore, it is observed from Fig. 6 that the random error, observed as scatter between individual data points, is larger for the batch adsorption–desorption method than it is for frontal analysis. This might be due to the use of a different resin sample and a different, manually prepared sugar solution for each data point of the isotherm. In addition sorption was quantified by a concentration measurement. Any unintended variation between contents or conditions of each flask and error in the concentration measurement contribute to the scatter. In contrast, the data obtained with frontal analysis are obtained from a single, larger batch of resin in a single column without errors resulting from the concentration measurement.

The glucose isotherm found in this work with frontal analysis is slightly lower at low concentration than found in [32] with a batch adsorption–desorption method for the same resin type. However, due to a stronger isotherm curvature found in this work, there is excellent agreement at high sugar concentration.

The glucose isotherm on Na^+ loaded resin obtained with frontal analysis and the column adsorption–desorption method are compared in Fig. 7. The isotherms from the two methods were in very close agreement. Scatter in the isotherm with the column adsorption–desorption method was low and similar to frontal analysis but lower than for the batch method. Isotherms obtained with the column adsorption–desorption method are as accurate as found by frontal analysis and it was found that there is no systematic difference between the two isotherms. However, frontal analysis is much less time consuming and fully automated. Therefore, the use of frontal analysis is recommended over the column adsorption–desorption method.

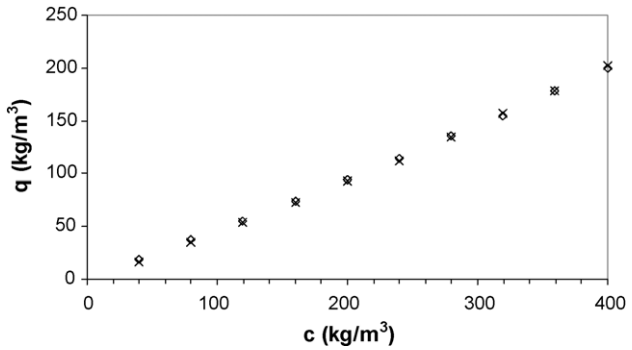

Fig. 7. Comparison of frontal analysis and column adsorption–desorption method for glucose isotherms on fine (200–400 mesh), 4% cross-linked resin in the Na^+ form, flow rate 10 cm^3/min, temperature 60 °C, (×) frontal analysis, (◊) column adsorption–desorption method.

4. Conclusions

Frontal analysis is a fast and accurate isotherm measurement method, which can be carried out automatically with standard HPLC equipment. It is suitable for routine sugar isotherm measurements on gel type cation-exchange resins under industrial processing conditions. The influence of shrinking of 4% cross-linked resin is shown to be so small that the resin volume can be conveniently assumed constant. Resin with a large particle size requires a decrease of the flow rate to ensure sharp breakthrough fronts. It was shown that the step series method is more prone to mass transfer resistance resulting in underestimation of the isotherm when the isotherm is measured over a wide concentration range typical for industrial conditions. Staircase frontal analysis produces isotherms, which show excellent agreement with isotherms measured with the column adsorption–desorption method and a reasonable agreement with the batch adsorption–desorption method. Staircase frontal analysis can be used for other types of sorbents as long as the tracer is truly non-retained, the breakthrough fronts are sharp, and sorbent shrinking that influences the isotherm is taken into account.

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