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COMPARISON OF STATIC AND DYNAMIC MEASUREMENTS OF ADSORPTION ISOTHERMS

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ABSTRACT

Adsorption isotherms can be determined experimentally by using either static or dynamic measuring methods. The adsorption behavior of the system dichloromethane–*n*-hexane on two normal-phase silica-gels was measured both statically by using the circulation method and dynamically by using the frontal analysis and the perturbation method. As a matter of conformity, adsorption excess isotherms, which are the results of static methods, should have to be converted into loading isotherms.

Analytical and different numerical conversion methods using different assumptions are presented and compared to each other. A conformity between the results of the analytical conversion method and the dynamically measured adsorption isotherms can be established if the decrease of the porosity with increasing loading is also taken into consideration.

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INTRODUCTION

For designing and simulating preparative liquid chromatographic separations, the knowledge of the adsorption isotherms of the system to be separated is necessary. To determine adsorption isotherms experimentally, different measuring methods are available, which are either static or dynamic.

Although both static and dynamic measuring methods are used for technical applications, comparisons of both kinds of measuring methods for the same system are rare and statements about their conformity contradictory:

In contrast to Wang et al. (1), who showed a good conformity to both kinds of measuring methods for the system hexane–hexanol on silica-gel, but who only examined a concentration range up to a weight fraction of hexanol of 0.03, Kehrer (2) found discrepancies of 10–40% for the system ethanol–water on different silica-gels depending on the flow rate and pore size of the adsorbents used.

After a description of the theoretical basis of static and dynamic measuring methods in sections "Static Measuring Methods" and "Dynamic Measuring Methods" with the necessary conditions to compare the results of both, the experimental setup will be described in section "Experiments." This will be followed by the results of the experiments, namely in section "Importance of the Porosity," the importance of the determination of the porosity and in section "Results," the results of comparing static and dynamic methods.

STATIC MEASURING METHODS

The Adsorption Excess

All static measuring methods are based on the idea of bringing a bulk phase with a known amount of substance n^0 and a known composition x_i^0 in contact with a dry solid adsorbent. After an isothermal formation of the adsorption equilibrium, the new composition x_i of the bulk phase is measured (see Fig. 1).

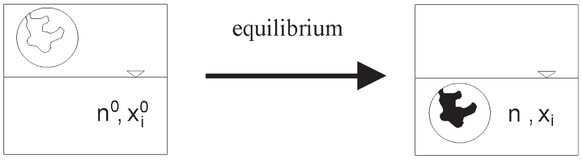

Figure 1. Principle of static measuring methods.

The static measurement gives a quantitative statement of which component of the bulk phase adsorbs preferably. However, a direct determination of the absolute adsorbed amount is not possible because neither the composition of the adsorbed phase nor the whole amount of the adsorbed substance can be measured. Therefore, the adsorption is described by the adsorption excess n_i^{E} which is defined as

$$n_i^{\mathrm{E}} = n^0(x_i^0 - x_i). \tag{1}$$

The adsorption excess is the surplus of component i in the real system compared to a hypothetic reference system with the same amount of substance n^0, but without adsorption (3). Using a mass balance on the whole adsorption system

$$n^0 = n + n' \tag{2}$$

where n' is the adsorbed amount of substance and n the amount of substance in the bulk phase, Eq. (1) can be rewritten in terms of properties of the adsorbed phase as follows:

$$n_i^{\mathrm{E}} = n'(x_i' - x_i). \tag{3}$$

Equation (3) is called the Ostwald–Izaguirre equation (4). It shows, that the adsorption excess is the amount of component i adsorbed reduced by the amount of component i that would be adsorbed if the composition of the adsorbed phase was the same as that of the bulk phase.

Conversion of Excess Properties into Adsorption Isotherms

While comparing the results of the static and dynamic measuring methods, it is necessary to convert the excess isotherms into adsorption isotherms, which represent the results of the dynamic measurements. For this purpose, different conversion methods are compared in order to obtain a quantitative statement about the discrepancies between them.

The aim of the conversion is to calculate the amount of substance of the stronger adsorbing component n_1' in a binary system which is defined as

$$n_1' = n'x_1'. \tag{4}$$

Introducing Eq. (4) into Eq. (3) with $i = 1$ leads to

$$n_1^{\mathrm{E}} = n_1' - \frac{n_1' x_1}{x_1'} \tag{5}$$

where neither n'_1 nor x'_1 are directly measurable, so there are two unknown physical properties. In order to solve Eq. (5), different methods are presented, where one offers an analytical solution, the others are based on equations found in literature which allow a calculation using numerical parameter fittings.

The Analytical Solution

For an analytical solution of Eq. (5), n'_1 can be evaluated only from the measured fluid composition if $n'_1 \gg n'_2$, so that the composition of the adsorbed phase can be assumed as

$$x'_1 = 1, \tag{6}$$

which means that only component 1 adsorbs. Using this assumption, Eqs. (1) and (3) can be used in order to calculate the adsorbed amount of substance by

$$n'_1 = n^0 - \frac{x_2^0 n^0}{x_2}. \tag{7}$$

To avoid the limiting condition that only one component adsorbs, methods based on numerical parameter fittings are used. Three methods have been found in the literature, which are able to convert an excess isotherm into a loading isotherm by using nothing but the measured excess data. Here, the aim is also to calculate the composition of the adsorbed phase x'_1 to obtain n'_1.

Method Based on Minka and Myers (5)

This method is based on the publication of Minka and Myers (5) and is described fully by Hirsch (3):

The composition of the adsorbed phase for component j can be calculated by (5):

$$x'_j = \frac{x_j K_{ij}}{\sum x_j K_{ij}} \tag{8}$$

with the properties of K_{ij}:

$$K_{ii} = 1 \quad \text{and} \quad K_{ij} = \frac{1}{K_{ji}} \tag{9}$$

Equation (8) can be rewritten for the binary case as:

$$x'_1 = \frac{x_1}{x_1 + x_2 K_{12}}. \tag{10}$$

The definition of x_1' is:

$$x_1' = \frac{n_1'}{n_1' + n_2'}. \tag{11}$$

The adsorbed amount of substance n' can be written easily in terms of the capacities of the adsorbent in moles of pure liquid b_1 and b_2, if it is assumed that the volume change is zero when the solution is formed in the micropores from the pure liquids (5):

$$\frac{1}{n'} = \frac{x_1'}{b_1} + \frac{x_2'}{b_2}. \tag{12}$$

Using Eqs. (11) and (12) and the derivation of the parameter K_{12} (5):

$$K_{12} = \exp\left(\frac{a_2}{b_2} - \frac{a_1}{b_1}\right) \tag{13}$$

whereby a_1 and a_2 are the free energies of immersion for components 1 and 2, Eq. (3) can be expressed specifically for the mass of adsorbent m_{ad} as:

$$\frac{n_1^{\mathrm{E}}}{m_{\mathrm{ad}}} = \frac{x_1 x_2 (1 - K_{12})}{\left(\frac{x_1}{b_1} + \frac{x_2}{b_2} K_{12}\right)}. \tag{14}$$

If the values of a_1, a_2, b$_1$, and b_2 are unknown, it is required to fit these parameters to measured excess isotherms. The Gurvitsch rule (6) is used, which states that the capacities of the adsorbent are reversed approximately proportional to the partial molar liquid volumes v_1 and v_2 of the two components, to reduce the number of parameters to three:

$$\frac{b_1}{b_2} \approx \frac{v_2}{v_1}. \tag{15}$$

Fitting K_{12} in Eq. (14) with a_1, a_2, b_1, and b_2 in Eq. (13) to the experimental data $(n_1^{\mathrm{E}}, m_{\mathrm{ad}})$ and introducing the result into Eq. (10) the specific adsorbed amount of component 1 is given by

$$\frac{n_1'}{m_{\mathrm{ad}}} = \frac{n_1^{\mathrm{E}}/m_{\mathrm{ad}}}{x_1' - x_1} x_1'. \tag{16}$$

Methods Based on Everett–Schay-Equation

The second method was described by Berger and Dekany (7), who used another approach:

In order to fit a function to the measured data of the adsorption excess, the Everett–Schay-equation (8–10) can be used, which is defined as

$$\frac{x_1 x_2}{n_1^{\mathrm{E}}} = \frac{1}{b_1}\left[\frac{r}{S-1} + \frac{S-r}{S-1}x_1\right] \tag{17}$$

where S is the separation factor of adsorption

$$S = \frac{x_1' x_2}{x_2' x_1} \tag{18}$$

and r the ratio of the molar liquid volumes:

$$r = \frac{v_2}{v_1}. \tag{19}$$

Using Eq. (17), the separation factor S and the adsorption capacity b_1 have to be fitted to the experimental data.

The composition of the adsorbed phase x_1' can either be calculated by using Eq. (18) or by the following procedure.

From geometric considerations the volume of the adsorbed phase V' can be described by:

$$V' = t'a' = n_1' v_1 + n_2' v_2 = b_1 v_1 \tag{20}$$

where t' is the thickness of the adsorbed phase and a' is the specific surface area of the adsorbent. With

$$n' = n_1' + n_2'. \tag{21}$$

Equation (20) is resolved to n' and substituted in Eq. (3), which leads to the composition of the adsorbed phase:

$$x_1' = \frac{r n_1^{\mathrm{E}} + x_1 V'/v_1}{V'/v_1 + n_1^{\mathrm{E}}(r-1)}. \tag{22}$$

Using either Eq. (18) or (22) for the calculation of the composition of the adsorbed phase x_1', the adsorbed amount n_1' is determined by using Eq. (16).

It can be resumed, that Eqs. (14) and (17) provide models for the representation of adsorption excess data, in which unknown parameters have to be fitted to experimental data. With these parameters it is possible to calculate the composition of the adsorbed phase x_1' with Eq. (10) for the model based on Minka and Myers (5), respectively Eqs. (18) or (22) for the model based on the Everett–Schay-Eq. (17).

The main difference between the numerical solutions by Minka and Myers (5) and Berger and Dekany (7) and the analytical solution of the conversion problem focuses on the boundary between the bulk and the adsorbed phase, what is shown and idealized in Fig. 2. The analytical solution assumes that the adsorbed phase consists exclusively of molecules of the stronger adsorbing component, but all molecules of the less adsorbing component are part of the bulk phase. So the volume of the adsorbed phase depends on the loading and therefore on the composition of the whole system and is therefrom variable.

In contrast to that modeling, the volume of the adsorbed phase is assumed to be constant over the whole concentration range in the numerical solutions and it includes amounts of both the components. The number of molecules in the adsorbed phase depends only on the molar volume of the mixture in the pores.

It is obvious that the analytical solution gives lower loadings of the stronger adsorbing component 1, because regarding the fact that the bulk phase's composition is measured, the more molecules of the less adsorbing component 2 are removed from the bulk phase, the more molecules of stronger adsorbing component 1 have to be adsorbed in order to keep the measured bulk phase's composition constant. The smaller the differences of the driving forces of adsorption between the two components, the less realistic the assumption of the analytical solution seems to be. But for great differences, it might be more realistic than the assumption of the numerical solution.

In Fig. 3, the different conversion methods from excess to loading isotherms have been compared. As can be seen, the analytical solution delivers lower loadings compared to the three numerical parameter-fitting methods, which show a good conformity to them. The use of the numerical solution with Eq. (14)

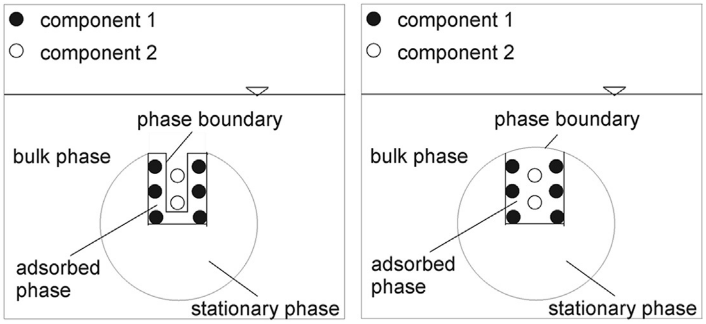

Figure 2. Assumed phase boundaries for the analytical (left) and the numerical (right) conversion methods.

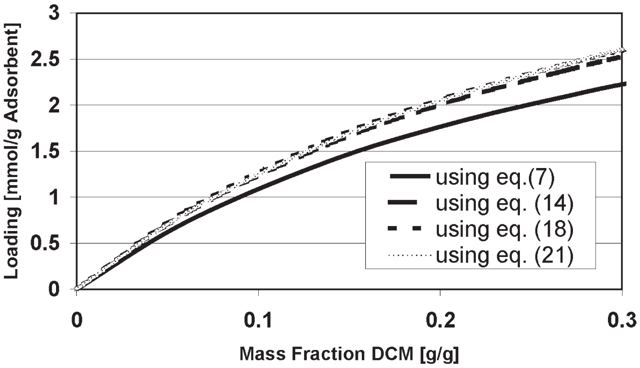

Figure 3. Comparison of different conversion methods based on the adsorption excess isotherm of the system DCM–*n*-hexane on Uetikon C-Gel C560 40–63 μm measured at 30°C.

compared to Eq. (18) leads to a maximum deviation of 2.3% in the examined concentration range.

DYNAMIC MEASURING METHODS

The Frontal Analysis

The frontal analysis (FA) is used in order to calculate the adsorbed amount q of a substance as a function of the concentration c using breakthrough curves. For this purpose, a chromatographic column, which is in adsorption equilibrium with the mobile phase at the concentration c^{I} and the loading q^{I}, is fed with a concentration step to the level c^{II} whereby the response signal $c(t)$ is recorded (see Fig. 4). The equilibrium loading q^{II} can be calculated using an integral mass

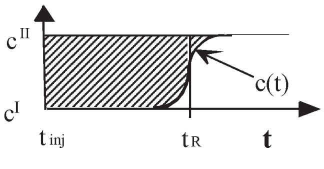

Figure 4. Frontal analysis.

balance of the chromatographic column

$$\epsilon V_{\mathrm{col}}(c^{\mathrm{II}} - c^{\mathrm{I}}) + (1 - \epsilon) V_{\mathrm{col}}(q^{\mathrm{II}} - q^{\mathrm{I}}) = \dot{V} t_{\mathrm{R}}(c^{\mathrm{II}} - c^{\mathrm{I}}) \tag{23}$$

where t_{R} is the retention time of the breakthrough curve and $\dot{V}$ the volume flow. The presence of the porosity ϵ and the volume of the column V_{col} in the mass balance clarify, that the loading is obtained in a volume-related dimension in contrast to the adsorption excess which is related to the mass of the adsorbent normally.

The Perturbation Method

Figure 5 shows the principle of the perturbation method (PM). To a chromatographic column which is equilibrated with the concentration c^n, a little perturbation is applied, and its retention time is measured. With the relationship

$$t_{\mathrm{R}}^{n}(c^{n}) = t_0 \left(1 + \frac{1 - \epsilon}{\epsilon} \left. \frac{\mathrm{d}q}{\mathrm{d}c} \right|_{n} \right), \tag{24}$$

where t_0 is the dead time of the column, it is possible to calculate the tangent slope $\mathrm{d}q/\mathrm{d}c$ of the adsorption isotherm (13). In order to calculate the whole isotherm, it is necessary to measure the retention times on different concentration levels. With these retention times a parameter fitting to the first derivative of an adsorption isotherm model is performed.

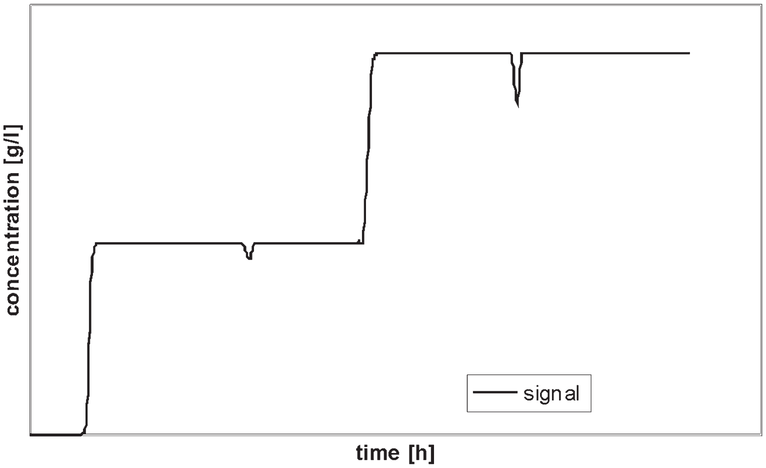

Figure 5. Perturbation method.

EXPERIMENTS

Selection of the Test System

Several requirements have to be followed in selecting the substances and stationary phases to be examined:

The stationary phase should not swell. Especially for the static measurements, it must be possible to dry the material by evacuation and heating. Therefore, two normal-phase silica-gels have been chosen for the experiments: Kromasil NP 10 μm 100A (supplied by Eka-Nobel) and Uetikon C-Gel C560 40–63 μm (supplied by Uetikon Chemie).

Further, the selected liquids have to satisfy the requirements of the static and the dynamic measurements as well.

The static measurements need substances which can be separated easily from the adsorbent by heating. For the determination of the composition using the density of the mixture, a density difference of at least 0.2 kg/L is desirable. Further, size exclusion has to be avoided.

For the dynamic measurements, the stronger adsorbing component has to have a good UV-response. The weaker adsorbing component shall be as unpolar and accordingly, weak adsorbing as possible, because the inability of a nonadsorbing tracer to displace adsorbed molecules of a more polar solvent is expected. Thus, the experimentally determined porosity could be too low.

All these specifications were satisfied by the system dichloromethane–*n*-hexane with dichloromethane (DCM) as the component which is much stronger adsorbed by the normal-phase silica-gels than *n*-hexane, which as an unpolar alkane is according to Meyer (14), one of the weakest adsorbing substances. The chemicals were supplied by Merck KGaA in LiChrosolv® quality.

Static Measurements

The static measurements were conducted using a circulation apparatus for the measurement of adsorption excess isotherms, which was developed and constructed at the Fachgebiet Thermodynamik und Thermische Verfahrenstechnik of the Technical University of Berlin.

The circulation apparatus is shown in Fig. 6. It consists of a fluid circulation, which is driven by a gear type pump model 8250/A251, supplied by Scherzinger. The whole apparatus is surrounded by an air bath which allows measurements up to 150°C. Inside the circulation a vibrating tube model DMA60 DMA602 HP, supplied by Anton Parr, densimeter is arranged. Using the densimeter it is possible to determine the composition of a binary mixture if the liquids have different densities. A further description of the apparatus can be found in Refs. (3,11).

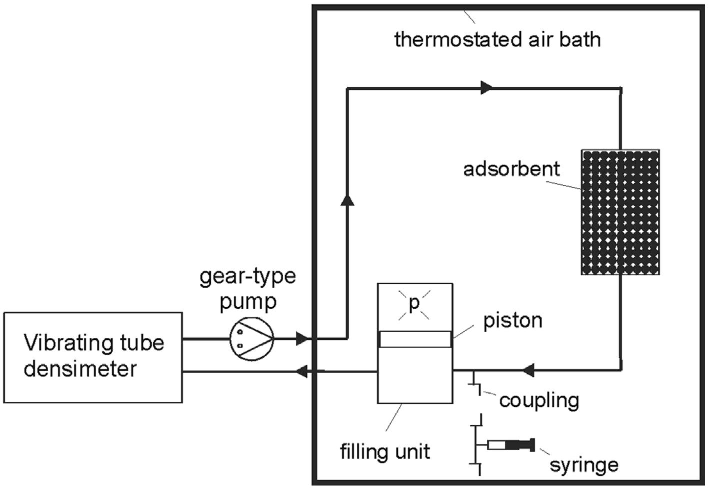

Figure 6. Basic scheme of the circulation apparatus.

To conduct the measurements after calibrating the densimeter, it is necessary to fill the evacuated filling unit with the desired amount of degassed substances with an accuracy of 0.001 g. The adsorbent is dried by evacuation and heated to 100°C. After starting the experiment, the circulation is sustained as long as the density of the mixture changes. When the value of the density keeps constant the adsorption equilibrium is reached.

A coupling, which can be connected to a syringe, gives the possibility to change the composition of the bulk phase in order to conduct a new experiment without emptying the whole system.

The measurements were conducted over the whole concentration range of the binary system DCM–*n*-hexane.

Dynamic Measurements

The dynamic measurements were conducted using a binary high-pressure gradient HPLC manufactured by Hewlett-Packard (Series 1100). The HPLC is equipped with a diode-array detector. For the measurement of the porosity with the tracer *n*-heptane, the HPLC was connected to a differential refractometer type 198.00 manufactured by Knauer.

The dynamic measurements were conducted using a chromatographic column with a length of 250 mm and a diameter of 10 mm. Before slurry-packing the column with the solvent *n*-hexane, the silica-gel was dried by evacuation and heated to 100°C in order to establish the same conditions in preparing the stationary phase for static and dynamic measurements.

The FA as well as the PM are used with concentrations up to 264 g/L DCM, which represents a range relevant for preparative chromatography. In this range, eight concentration levels were investigated.

To compare the static and dynamic methods, the result is expressed by the molar amount of the stronger adsorbing component DCM per mass of adsorbent, using:

$$n_1' = \frac{q_1 V_{\mathrm{ads}}}{m_{\mathrm{ads}} M_1} = \frac{q_1 (1 - \epsilon) V_{\mathrm{col}}}{m_{\mathrm{ads}} M_1} \tag{25}$$

where M_1 is the molar mass of DCM, m_{ads} the mass, and V_{ads} the volume of the adsorbent in the chromatographic column.

Determination of the Porosity

As can be seen in Eqs. (23) and (24), the determination of the porosity plays an extremely important role for the dynamic determination of adsorption isotherms. Since both components are fully pore filling, it is necessary to determine the true porosity which means the open pore and the interstitial volume. A tracer should be used, which is full pore filling, but does not adsorb. Since the adsorption on normal-phase silica-gels depends on the polarity, a substance is needed, which is as nonpolar as *n*-hexane, like *n*-heptane (12).

First, the porosity is measured by injecting the tracer *n*-heptane on the unloaded column filled with the pure solvent *n*-hexane by

$$\epsilon = \frac{t_{\mathrm{R}} \dot{V}}{V_{\mathrm{col}}}. \tag{26}$$

In this work, the porosity of a pre-loaded column at different concentration levels has been determined at different DCM-concentrations, also. The porosity evaluated from these measurements is subsequently named as effective porosity. It is evaluated at different concentration levels of the adsorbing component. The results and their consequences are shown and discussed in section "Importance of the Porosity."

IMPORTANCE OF THE POROSITY

Results of the Porosity Measurements

Figure 7 shows that the effective porosity decreases with the increasing concentration of DCM. This is valid for the Kromasil and the Uetikon normal-phase silica-gel.

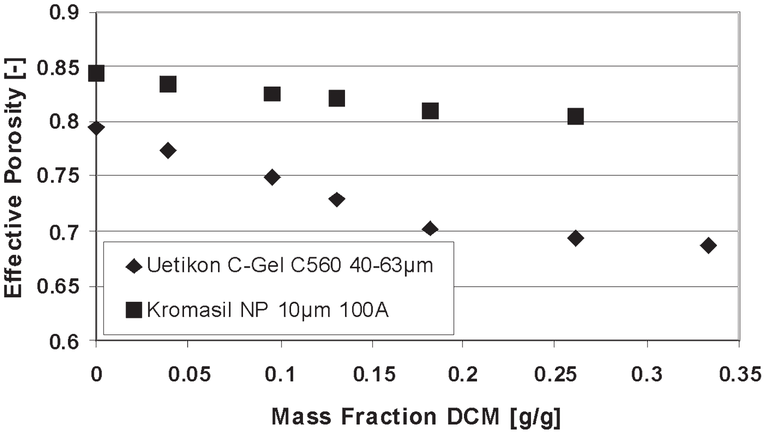

Figure 7. Porosity on different concentration levels (tracer: *n*-heptane, 30°C).

Figures 8 and 9 show an interpretation of this effect. In Fig. 8, the unloaded column is filled with the pure solvent *n*-hexane. The volume of the column is divided into the volume of the liquid and the adsorbent. After the adsorption of the DCM, the volume, which is accessible to the mobile phase reduces by the volume of the adsorbed phase consisting of DCM (Fig. 9).

Consequences for the Evaluation of the Dynamic Measurements

Using the decreasing effective porosity shown in Fig. 7 for the evaluation of the FA, the mass balance represented by Eq. (23) has to be rewritten formally as

$$\epsilon_{\mathrm{eff}}^{\mathrm{II}} V_{\mathrm{col}}(c^{\mathrm{II}} - c^{\mathrm{I}}) + (1 - \epsilon_{\mathrm{eff}}^{\mathrm{II}}) V_{\mathrm{col}}(q_{\mathrm{eff}}^{\mathrm{II}} - q_{\mathrm{eff}}^{\mathrm{I}}) = \dot{V} t_{\mathrm{R}}(c^{\mathrm{II}} - c^{\mathrm{I}}) \tag{27}$$

where $\epsilon_{\mathrm{eff}}^{\mathrm{II}}$ is the effective porosity and $q_{\mathrm{eff}}^{\mathrm{II}}$ the resulting loading on the respective concentration level.

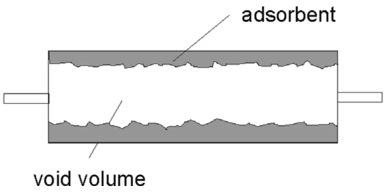

Figure 8. Unloaded column.

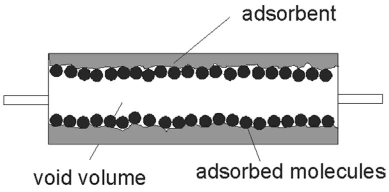

Figure 9. Loaded column.

For every concentration step the increase of loading has to be calculated by resolving Eq. (27):

$$q_{\mathrm{eff}}^{\mathrm{II}} - q_{\mathrm{eff}}^{\mathrm{I}} = \Delta q_{\mathrm{eff}} = \frac{\dot{V} t_{\mathrm{R}}(c^{\mathrm{II}} - c^{\mathrm{I}}) - \epsilon_{\mathrm{eff}}^{\mathrm{II}} V_{\mathrm{col}}(c^{\mathrm{II}} - c^{\mathrm{I}})}{(1 - \epsilon_{\mathrm{eff}}^{\mathrm{II}}) V_{\mathrm{col}}}. \tag{28}$$

Equation (28) gives the loading increase related to the volume of the stationary phase. The loading increase for the whole chromatographic column is given by

$$\Delta q_{\mathrm{eff,col}} = \Delta q_{\mathrm{eff}} V_{\mathrm{ads}} = \Delta q_{\mathrm{eff}} (1 - \epsilon_{\mathrm{eff}}^{\mathrm{II}}) V_{\mathrm{col}} \tag{29}$$

where V_{ads} is the volume of the stationary phase including the adsorbed molecules. This has to be done in order to fulfill the mass balance. The loading of the column for each concentration level is given by

$$q_{\mathrm{eff,col}}^{\mathrm{II}} = q_{\mathrm{eff,col}}^{\mathrm{I}} + \Delta q_{\mathrm{eff,col}}. \tag{30}$$

To obtain a comparability with the results of the static measurements, it is necessary to convert this loading to the molar adsorbed amount related to the mass of adsorbent by

$$n_1' = \frac{q_{\mathrm{eff,col}}^{\mathrm{II}}}{m_{\mathrm{ads}} M_1} \tag{31}$$

where m_{ads} is the mass of adsorbent in the chromatographic column and M_1 the molar mass of component 1, in this case of DCM.

The PM is evaluated by using Eq. (24) with the effective porosity specific for each concentration level. Comparable to the evaluation of the FA and in contrast to the usual evaluation of the PM, the change of the volume related loading up to the nth concentration level is calculated using

$$\Delta q_{\mathrm{eff}}^{n} = q_{\mathrm{eff}}^{n} - q_{\mathrm{eff}}^{n-1} \tag{32}$$

where q_{eff}^{n} is the loading on the respective concentration level and q_{eff}^{n-1} the loading on the next lower concentration level. The conversion of the volume specific loading increase to the loading increase of the whole column is calculated similar to Eq. (29) by using

$$\Delta q^{n}_{\mathrm{eff,col}} = \Delta q^{n}_{\mathrm{eff}} V_{\mathrm{ads}} = \Delta q^{n}_{\mathrm{eff}}(1 - \epsilon^{n}_{\mathrm{eff}})V_{\mathrm{col}}. \tag{33}$$

The calculation of the loading of the whole column is done with

$$q^{n}_{\mathrm{eff,col}} = q^{n-1}_{\mathrm{eff,col}} + \Delta q_{\mathrm{eff,col}} \tag{34}$$

and the adsorbed amount is given by:

$$n'_1 = \frac{q^{n}_{\mathrm{eff,col}}}{m_{\mathrm{ads}} M_1}. \tag{35}$$

RESULTS

In the following, the adsorption isotherms obtained with the different measuring methods are plotted and compared with each other. The isotherms are shown for a DCM-concentration from 0 to 264 g/L, which is equivalent to a mass fraction DCM of about 0.33.

Figure 10 shows the adsorption isotherms of the static measurements and the FA, Fig. 11 of the static measurement and the PM, both for the adsorbent Kromasil expressed in mmole per g adsorbent plotted against the mass fraction of DCM. The isotherm assuming constant porosity shows a good conformity

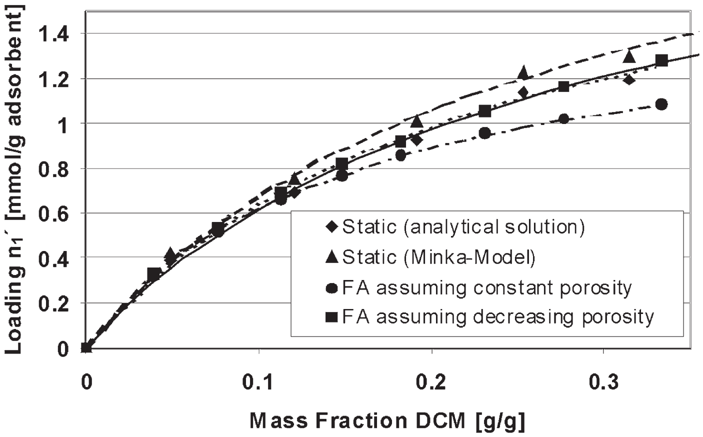

Figure 10. Adsorption isotherms of DCM–*n*-hexane at 30°C on Kromasil 10 μm 100 A normal-phase silica-gel measured with the static method and the FA.

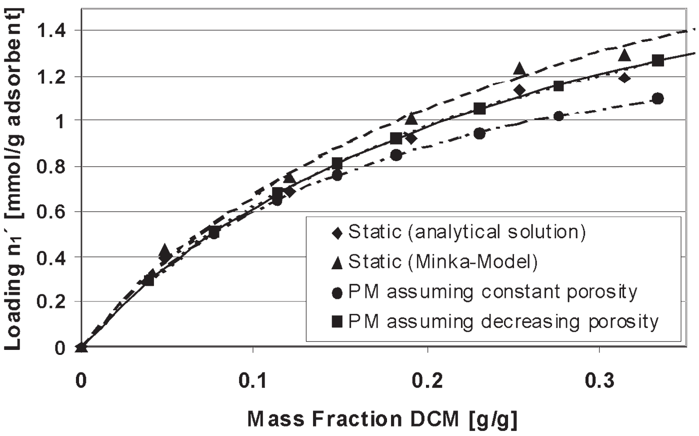

Figure 11. Adsorption isotherms of DCM–*n*-hexane at 30°C on Kromasil 10 μm 100 A normal-phase silica-gel measured with the static method and the PM.

between the isotherm of the static method and the results of the FA as well as of the PM for low concentrations, only. For increasing DCM concentrations, the discrepancies between the isotherms of the static and dynamic methods increase. If the DCM load depending effective porosity is used for the evaluation of the dynamic methods, a good agreement between the results of the FA and the perturbation on the one hand and the analytical solution of the static excess isotherm data on the other hand can be reached, but there are still discrepancies to the numerical solution of the conversion of about 6.3% for the FA and 4.7% for the PM.

A similar effect can be observed in the adsorption isotherms on Uetikon shown in Figs. 12 and 13, but the descripancies to the numerical solution are greater, namely 13.5% for the FA and 11.5% for the PM.

CONCLUSION

As can be seen in the previous section, it is possible to establish a conformity between a static measuring method on the one hand, and the dynamic measuring methods FA and PM on the other hand. To gain this conformity in the conducted experiments, three conditions have to be fulfilled:

- The decrease of the effective porosity with increasing loading has to be taken into consideration during the evaluation of the dynamic measuring methods.

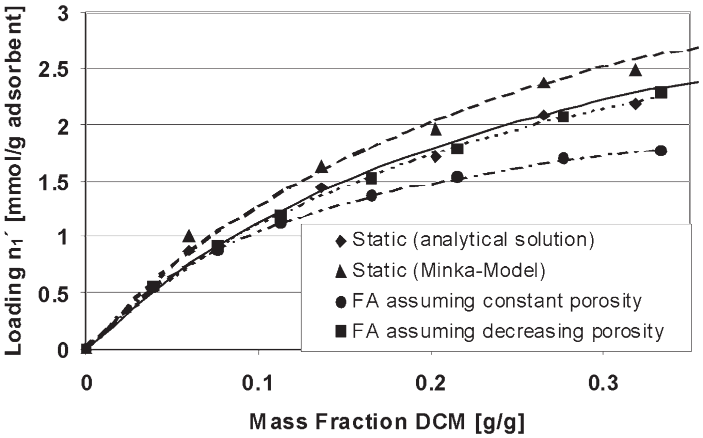

Figure 12. Adsorption isotherms of DCM–*n*-hexane at 30°C on Uetikon C-Gel C560 40–63 μm normal-phase silica-gel measured with the static method and the FA.

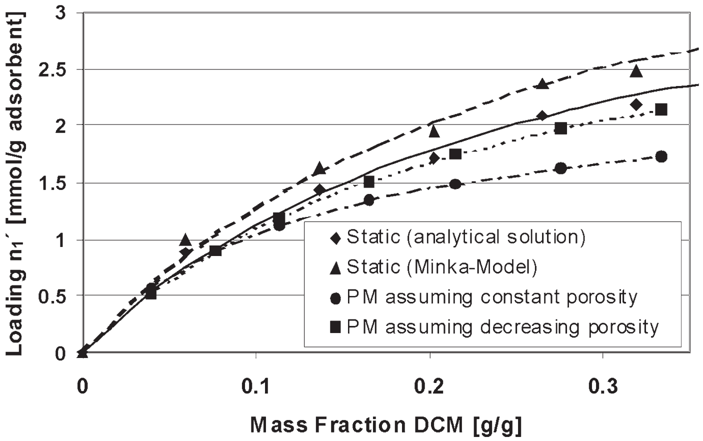

Figure 13. Adsorption isotherms of DCM–*n*-hexane at 30°C on Uetikon C-Gel C560 40–63 μm normal-phase silica-gel measured with the static method and the PM.

- The stationary phase used in both static and dynamic measurements have to be prepared in a similar way, namely it has to be dried by heating and evacuation, and contacts with liquids except the solvents used (DCM and *n*-hexane) have to be avoided.
- The excess data is evaluated using the analytical solution including the assumption that the adsorbed phase consists only of stronger adsorbing DCM and all hexane molecules are part of the flowing bulk phase. Caused by the very nonpolar character of hexane and the strong driving force of adsorption of DCM, this assumption has a realistic character for the particular systems.

From the results obtained, two important conclusions can be drawn:

- It is possible to measure pure thermodynamics by using dynamic measurements as well as using static methods. In the examined systems, the respective porosity for every experimental point has to be taken into consideration.
- If adsorption isotherms are needed for chromatographic applications in a volume related unit, their determination using static methods has two significant disadvantages. By converting the measured excess data into loading isotherms, the discrepancies between different conversion methods have to be taken into consideration. On this field, further research seems to be necessary. The other point is, that for the conversion of excess into volume-related isotherms, the porosity as a function of the loading has to be known.

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