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ADSORPTION EQUILIBRIA FROM SUPERCRITICAL SOLUTIONS

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This work focuses on the adsorption equilibria of dissolved components from supercritical solutions onto stationary chromatographic phases. Adsorption isotherms for single solutes as well as mixtures were determined experimentally at various pressures using a supercritical fluid chromatographic setup. In addition, influence of temperature and mobile phase composition on the adsorption was investigated.

INTRODUCTION

Adsorption isotherms are a major basis for design and optimisation of all adsorptive processes. Chromatography is of increasing importance in the production of fine chemicals. Using supercritical fluids as mobile phases has the advantages of lower viscosities and easier product recovery. For development and design of a chromatographic process or for simulation of chromatography, e.g. for design of a Simulated Moving Bed process, the knowledge of adsorption isotherms is one of the most important requirements. For other applications, e.g. for regeneration of solvents used in Supercritical Fluid Extraction by adsorption, the adsorption respectively desorption equilibrium under supercritical conditions is of fundamental importance, too.

For the determination of adsorption isotherms an experimental equipment has been built. It consists of a fluid preparation and two chromatographic units with UV detector and pressure expansion. The equipment allows the performance of peak experiments, frontal analysis, and perturbation experiments. As stationary phase commercial analytical HPLC-phases are used.

Binary adsorption equilibria of α -tocopherol and δ -tocopherol were determined. Within the group of vitamin E, α -tocopherol has the highest vitamin activity. Its anti-oxidative properties lead to a stabilization against other hormones and enzymes. In extracts from natural sources, all tocopherols are present. A separation allows the gaining of the most valuable component.

Pressure, composition of the mobile phase, and the adsorbent material were varied. Results obtained by different measurement methods were compared. From experimental data, coefficients of mixture adsorption models could be obtained. Using these models, it was possible to simulate the behaviour of chromatographic processes.

MATERIALS AND METHODS

Carbon dioxide was obtained from KWD (Bad Hönningen, Germany) with a purity of more than 99.95%. Isopropanol (IPA; > 99.95%), used as modifier and n-hexane (> 99.99%) were purchased from Merck (Darmstadt, Germany). The columns were packed with Nucleosil, 5 μm particles, 100 \AA pores (Macherey-Nagel, Germany) respectively Kromasil, 10 μm Particles, 60 \AA pores (Eka Chemicals, Bohus, Sweden). α -tocopherol (99%) was obtained from Calbiochem, San Diego, USA. δ -tocopherol (96%) was obtained from ICN Biomedicals, Eschwege, Germany.

The apparatus for the determination of adsorption isotherms is shown in figure 1. Liquid carbon dioxide is compressed up to 40 MPa by a pneumatically driven pump. This process is carried out in modified PM-101 module (NWA; Lörrach, Germany). The flow of liquefied carbon dioxide is divided into two streams. Stream A is used for the adsorption measurements, stream B is used for the determination of concentrations during perturbation experiments. In both flows, pressures are lowered to operating pressure by pressure reducing valves. With (260D, Isco, Lincoln NE, USA) carbon dioxide stream A is kept at a constant flow rate. With two double head HPLC pumps (Gynkotec, Germering, Germany and Knauer, Berlin, Germany) and another syringe pump liquid modifier and a feed solution can be added to the carbon dioxide. Operating temperature is achieved with a heating cabinet (Binder, Germany) containing the columns and five 6-port Rheodyne valves. For adsorption and concentration determination analytical chromatographic columns (4.6 x 250 mm) are used. After detection with UV detectors (LCD, GAT, Germany and SPD6, Shimadzu, Japan), the pressure is reduced to ambient pressure. Gas flows are measured with gas meters.

The apparatus allows the measurement of adsorption isotherms with peak analysis, frontal analysis, and a perturbation method. The second chromatographic unit allows the performance of perturbation experiments and the analysis of the concentration level in one step. Operating conditions can be set up to a maximum of 350 K and 30 MPa.

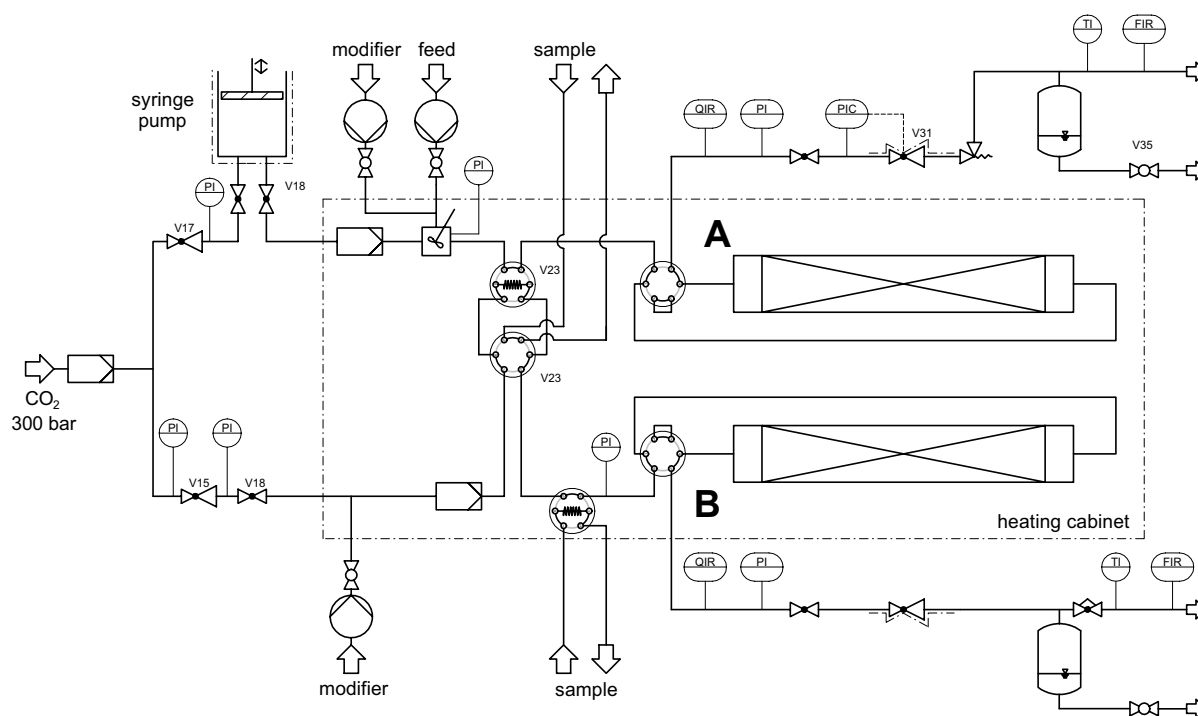


Figure 1 : Apparatus for the determination of adsorption isotherms

DESCRIPTION OF ADSORPTION EQUILIBRIA

Adsorption equilibria from supercritical solutions are described like adsorption equilibria from liquids. For pure component adsorption all standard isotherms as Langmuir and BET can be applied. A versatile isotherm for various systems is the Hill-isotherm (equation 1). This isotherm was obtained from statistical thermodynamics [1] and can be fitted to a wide range of adsorption equilibria. For $n = 1$ the isotherm is identical to the Langmuir isotherm. For $n \geq 2$ it is possible to describe inflection points. In this study the Hill isotherm in a cubic form is used.

$$q = \frac{q_s}{n} \cdot \frac{b_1 \cdot c + 2 \cdot b_2 \cdot c^2 + \dots + n \cdot b_n \cdot c^n}{1 + b_1 \cdot c + b_2 \cdot c^2 + \dots + b_n \cdot c^n} \quad (1)$$

For describing the competitive adsorption the ideal adsorbed solution theory is used. This theory is a thermodynamic evaluation of competitive adsorption and can be used for gases [2] as well as for liquid [3] and supercritical solutions. The IAST allows the prediction of competitive adsorption solely from pure component isotherms. All thermodynamically consistent isotherms can be applied. The IAST is successfully for many systems behaving not too far away from ideality [4].

EXPERIMENTS

Isotherms were determined using perturbation chromatography [5]. This method extends analytical chromatography, which only determines retention times, to higher concentrations. For performing a perturbation experiment, the column is equilibrated at a constant concentration level. After reaching equilibrium, retention times of small perturbations are determined. As only small deviations from equilibrium occur, the equilibrium theory of chromatography can be used for calculations. From retention time at different concentration levels the isotherm derivative is calculated using equation 2. Main advantage of this method is its capability of analyzing mixtures. Furthermore, it does not require a detector calibration.

$$t_R = t_M \left(1 + \frac{1 - \varepsilon}{\varepsilon} \frac{dq}{dc} \right) \quad (2)$$

RESULTS

Pure component and competitive adsorption was determined on Nucleosil at 313 K and pressures of 16.1, 20.0, and 26.1 MPa, respectively. Mobile phase was carbon dioxide with 5 wt.-% of isopropanol. Feed concentration was increased until reaching detection limit. For each pure component isotherm at least 10 concentration levels were analysed. Cubic Hill isotherms were fitted to the experimental data. The adsorption isotherms for both tocopherols show an unusual anti-Langmuir behaviour. This means, that adsorbate-adsorbate interactions are stronger than adsorbate-adsorbent interactions. All isotherm parameters and goodness of fit are shown in table 1. The isotherms are shown in figure 2.

$q = \frac{q_s \cdot b_1 \cdot c + 2 \cdot b_2 \cdot c^2 + 3 \cdot b_3 \cdot c^3}{3 \cdot (1 + b_1 \cdot c + b_2 \cdot c^2 + b_3 \cdot c^3)}$					
Overall porosity: $\varepsilon = 0.8151$					
	q_s [mg ml ⁻¹]	b_1 [ml mg ⁻¹]	b_2 [ml ² mg ⁻²]	b_3 [ml ³ mg ⁻³]	r^2
α , 16.1 MPa	6.805e+4	3.811e-4	3.262e-12	3.210e-6	0.9926
α , 20.0 MPa	3.967e+4	4.864e-4	5.537e-6	1.693e-6	0.9967
α , 26.1 MPa	2.630e+3	5.483e-3	8.487e-5	7.223e-6	0.9976
δ , 16.1 MPa	9.102e+4	4.825e-4	1.584e-9	6.435e-6	0.9836
δ , 20.0 MPa	4.863e+4	6.629e-4	8.538e-6	2.630e-6	0.9935
δ , 26.1 MPa	6.755e+3	3.648e-3	5.971e-5	7.298e-6	0.9982

Table 1 : Isotherm parameters and goodness of fit for α , δ -tocopherol on Nucleosil

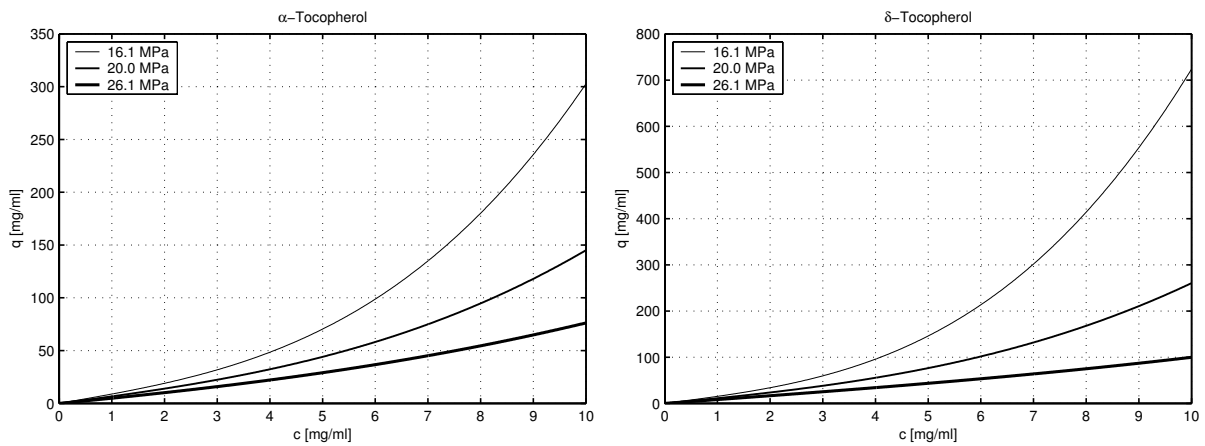


Figure 2 : Adsorption isotherms for α , δ -tocopherol on Nucleosil

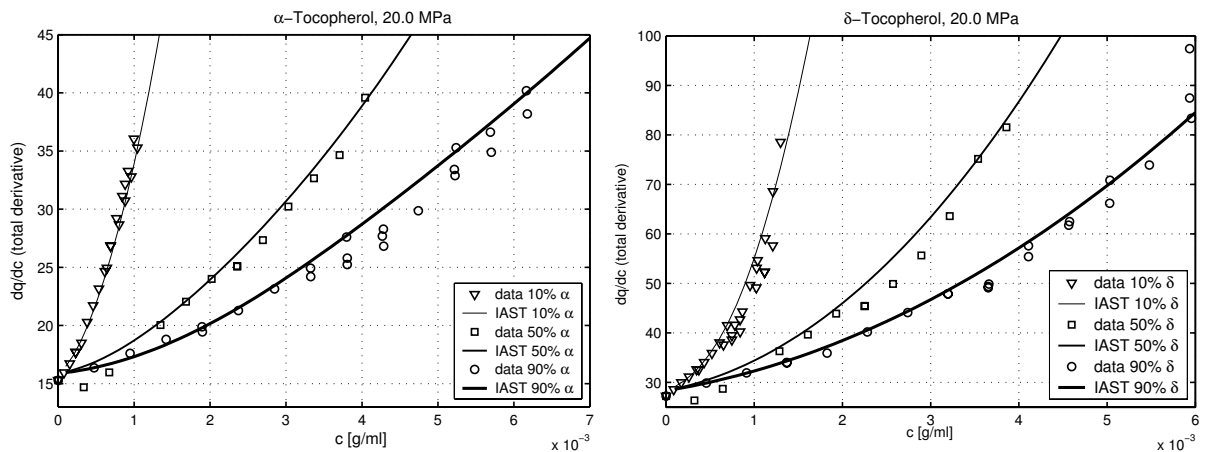


Figure 3 : Measured and predicted adsorption derivatives of mixture at 20 MPa

For the analysis of competitive adsorption feed mixtures with 10%, 50% and 90% α -tocopherol were prepared. Experimental conditions were identical to pure component experiments. From perturbation peak retention times apparent isotherm derivatives for both

components were calculated. These were compared to IAST predictions from pure component isotherms. All predictions were in good agreement with the data. In figure 3 experiments and IAST predictions at 20 MPa are shown.

In addition to the isotherm determination, modifier and temperature influence on linear adsorption coefficients (Henry coefficients) were analysed. These experiments were carried out in a HP SFC unit (Agilent, Waldbronn, Germany) using Kromasil as adsorbent. Results at 16 MPa and 25 MPa are shown in figure 4. At higher modifier contents solubilities in the fluid are increasing, therefore adsorption is decreasing. At higher temperatures adsorption is increasing. This behaviour is probably mainly caused due to density changes. At higher pressures density changes are smaller so temperature has less influence on adsorption.

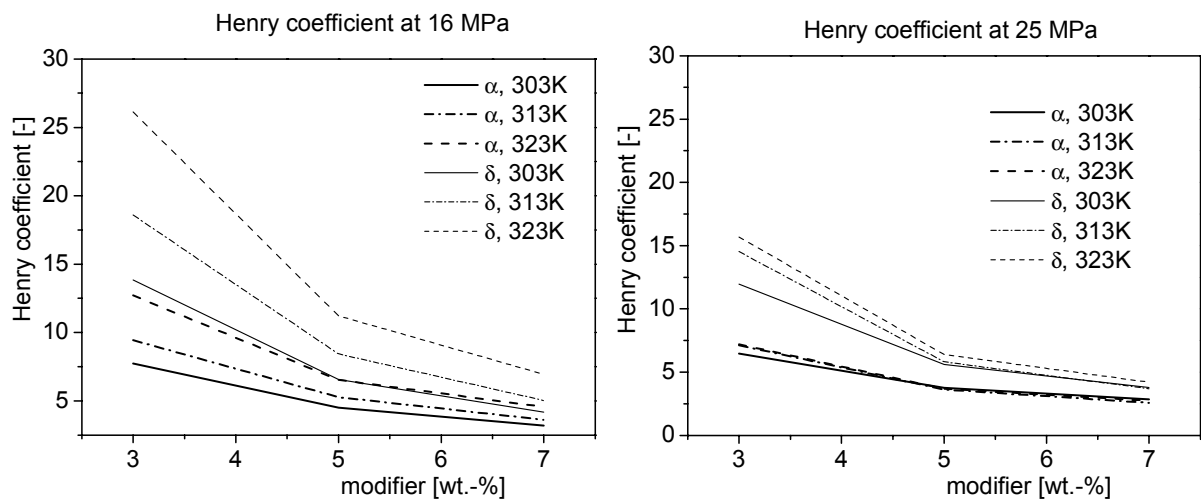


Figure 4: Modifier and temperature influence on adsorption for α , δ -tocopherol on Kromasil

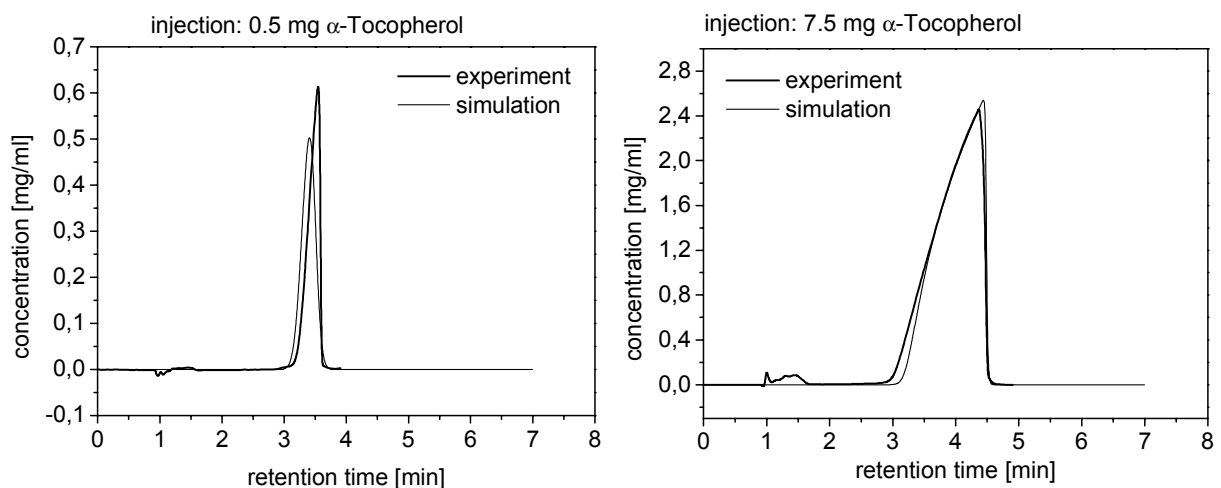


Figure 5 : Measured and simulated chromatograms for α -tocopherol on Kromasil

Portability of isotherms determined by perturbation chromatography had to be checked. This was done by simulating elution chromatograms using a simulation engine for supercritical fluid chromatography [6]. In order to get concentration vs. time data from the experiments, a

detector calibration was performed. Figure 5 shows chromatograms of small and large injections of pure α -Tocopherol on a Kromasil stationary phase. All simulated chromatograms are in good agreement with the experiments.

CONCLUSIONS

The results presented here illustrate the complex nature of adsorption equilibria. As a prediction of adsorption isotherms under supercritical conditions remains impossible, methods for fast and reliable experimental analysis are of key importance for design and optimisation of adsorption and chromatographic processes. Apparatus and methods presented in this study provide a basis for further investigations.

NOMENCLATURE

c	mobile phase concentration	kg/m^3
q	stationary phase loading	kg/m^3
t_R	retention time	s
t_M	hold-up time	s
b_n, q_s	isotherm parameters	
ε	overall porosity	

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