

Multi-component adsorption equilibria from sub- and supercritical fluid phases

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The recovery of pure substances from natural materials is of increasing interest. For this purpose the application of adsorptive separation processes is feasible and often necessary. In this study adsorption equilibria at higher pressures are investigated systematically. Data obtained can be applied for the design and modelling of adsorption processes from a supercritical phase, e.g. for supercritical fluid chromatography.

The adsorption equilibria of β -carotene in supercritical carbon dioxide with modifier and for the first time in subcritical propane were studied on different adsorbents with a chromatographic method. The experimental results were correlated with linear adsorption isotherms, since so far the concentrations in the fluid phase were low. Regarding adsorption equilibrium of β -carotene on C18 modified silica gel in CO₂ with 2-propanol as modifier, the loading decreases with increasing modifier concentration and increasing pressure. For the adsorption equilibrium of β -carotene on C18 modified silica gel in propane, the loading achieved is lower by two orders of magnitude. This is due to the much higher solubility of β -carotene in propane compared to CO₂.

Furthermore, the influence of modifier in CO₂ on adsorption equilibrium of α - and δ -tocopherol on silica gel was determined. The experimental results of pure substances were described with cubic Hill-isotherms. The mixture adsorption equilibrium was predicted with the Ideal Adsorbed Solution Theory (IAST).

INTRODUCTION

The recovery of pure substances from natural materials is of increasing interest. Therefore the application of adsorptive separation processes is feasible and often necessary [1]. For the operation and development of adsorption processes, especially for multi-component systems with supercritical solvents like CO₂ or subcritical solvent like propane, the knowledge of adsorption and desorption equilibrium data is of fundamental importance. Since the prediction of adsorption equilibrium data is still insufficient the experimental determination of phase equilibrium data within a wide range is indispensable. Tocopherol is one of the most important phytonutrients in edible oils. Tocopherols are well recognized for their antioxidative effect. Carotenoids, in particular β -carotene, have long been known for their provitamin A activity, as they can be transformed into vitamin A in vivo. In this work adsorption equilibria of α -tocopherol, δ -tocopherol [2, 3], and β -carotene, on different adsorbents were determined experimentally and modelled for pure and mixed components with supercritical CO₂ and subcritical propane as fluid phase. As the solubilities of these phytonutrients are much higher in propane than in supercritical CO₂ [4], the adsorption processes can be carried out at lower pressure, with less solvent, and without modifier. On the basis of the determined single component isotherms mixture adsorption can be predicted using the Ideal Adsorbed Solution Theory (IAST) [5].

MATERIALS AND METHODS

The experimental set-up consisting of two SFC units A and B presented by Lübbert [2] is shown in Figure 1. The equipment allows the performance of peak experiments (injecting samples onto an empty column), perturbation experiments (perturbing the equilibrium in a saturated column) as well as solubility measurements. Liquid carbon dioxide is compressed by a pneumatic pump (30 MPa) and delivered into the two chromatographic units. Unit A is used for the perturbation experiments. During experimental analysis, unit A is supplied with carbon dioxide by a syringe pump (260D, ISCO, Lincoln, NE, USA) to adjust a constant volume flow rate. Modifier is added to unit A by a second syringe pump (260D, ISCO, Lincoln, NE, USA). A feed solution can be added by a HPLC-pump (K1001, Knauer, Berlin, Germany). Perturbations are detected by an UV-detector (SPD-10A, Shimadzu, Kyoto, Japan). The pressure in unit A is adjusted by a controlled valve (V31). Samples for perturbation are injected manually through an injection valve. Unit B is used to analyse the concentration plateau in unit A by a switching valve (V23). Modifier is added by a HPLC-pump (HPP M300, Gynkotek, Germering, Germany). Pressure is controlled by a back pressure valve (V15). The flow rate is controlled by a depressurisation unit (V27 and V28). The concentration is detected by a UV-detector (LCD 503, GAT, Bremen, Germany).

Unit B is used to analyse the concentration plateau in unit A by a switching valve (V23). Modifier is added by a HPLC-pump (HPP M300, Gynkotek, Germering, Germany). Pressure is controlled by a back pressure valve (V15). The flow rate is controlled by a depressurisation unit (V27 and V28). The concentration is detected by a UV-detector (LCD 503, GAT, Bremen, Germany).

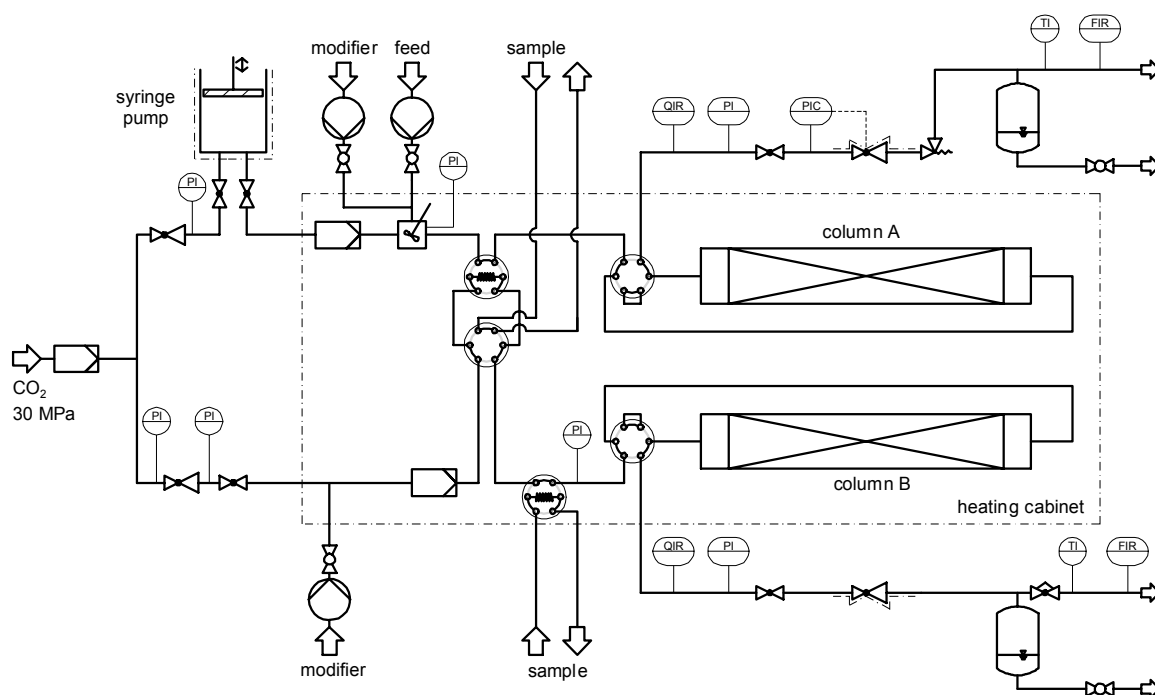


Figure 1: Schematic sketch of the experimental set-up

RESULTS AND DISCUSSION

Solubility

The solubility of β -carotene in propane was measured for different pressures and temperatures and the results are shown in Figure 2. With increasing temperature and pressure, solubility of β -carotene increases. The solubility of β -carotene under the measured condition

ranges from 100 to 450 $\text{mg}_{\beta\text{-caro}}/\text{kg}_{\text{propane}}$. These values are two orders of magnitude higher than the solubility of β -carotene in supercritical CO_2 [6] or in supercritical CO_2 with modifier .

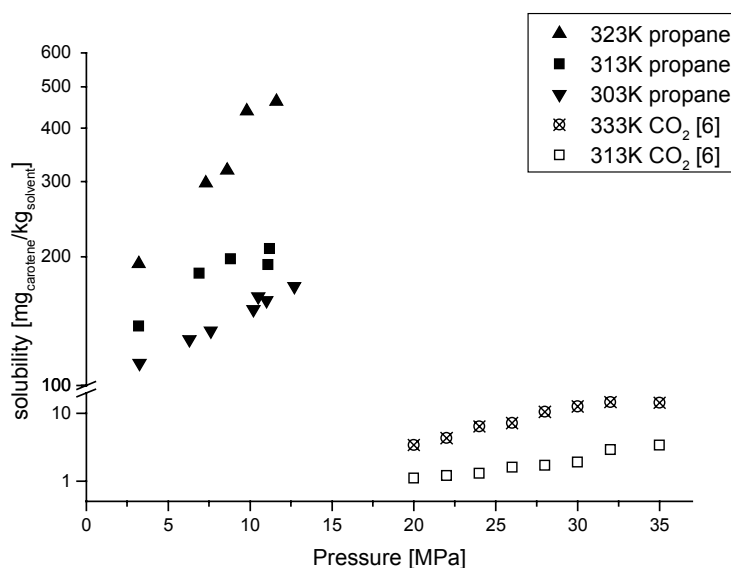


Figure 2:
Solubility of β -carotene in propane and in CO_2 [6] at different temperatures as a function of pressure

Single component adsorption

The adsorption behavior of β -carotene on Nucleosil 100-5- C_{18} was studied by the peak maximum method. The measured data fit well to linear adsorption isotherms as shown in Figure 3. With an increase in the modifier concentration, the loading decreases. It also shows that the loading is higher at lower pressure.

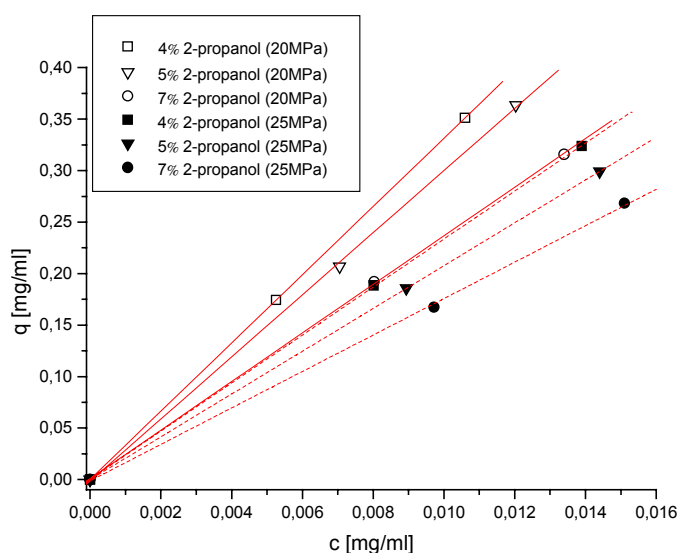


Figure 3:
Influence of pressure and modifier concentration on β -carotene isotherms with CO_2 /2-propanol at $T=313\text{ K}$ on Nucleosil 100-5- C_{18}

The adsorption isotherms obtained with propane and with CO_2 as fluid phase on Kromasil KR100-5- C_{18} are compared, as shown in Figure 4. A significant difference in loading with propane and with CO_2 as fluid phase was found and a decreasing loading with increasing solubility in the fluid phase was observed. The solid straight line represents the solubility of

β -carotene in CO_2 at $p=28$ MPa and $T=323$ K with 10% ethanol as modifier [7]. The dashed straight line represents the solubility of β -carotene in a solvent consisting of 50% propane and 50% ethane at $p=15$ MPa and $T=333$ K [8]. It is expected that the adsorption isotherms will follow the linear trend up to the solubility limit. The loading could be increased with lowered solubility of β -carotene in the fluid phase. This would be the case if a mixture of propane/ CO_2 instead of pure propane is used as fluid phase. However, this would result in a lower solubility of the fluid phase and thereby set a limit to the adsorbent loading. In other words, a compromise must be met between solubility and loading. Another way to achieve higher adsorbent loading would be the application of other adsorbents, such as bleaching earth or synthetic polymer resin adsorbents.

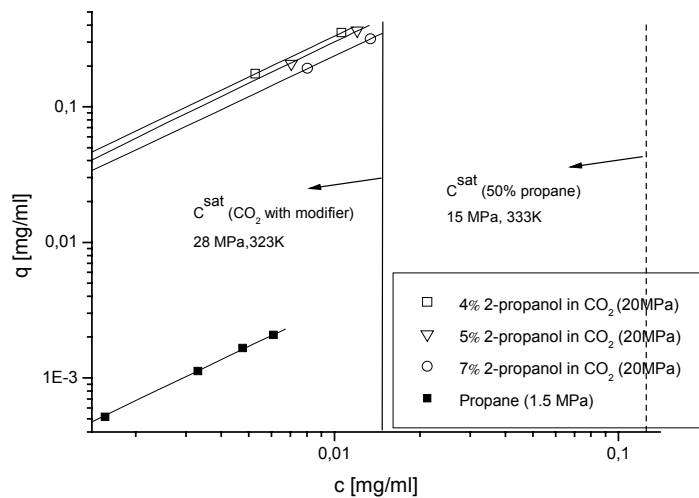


Figure 4:
Comparison of β -carotene isotherms on Kromasil KR100-5-C18 with CO_2 /2-propanol and with propane

The isotherms of α -tocopherol on Kromasil KR60-10SIL are shown in Figure 5 for different modifier concentrations of 2-propanol in CO_2 at $T=313$ K. The experimental data were correlated with a cubic Hill-isotherm. The isotherms show an unusual anti-Langmuir behavior which was already mentioned by Lübbert et al. [2]. The solid line indicates the region, where the fitted isotherms are based on measured data [3]. The decrease of the slope with increasing modifier concentration is related to an increased solubility of the components in carbon dioxide.

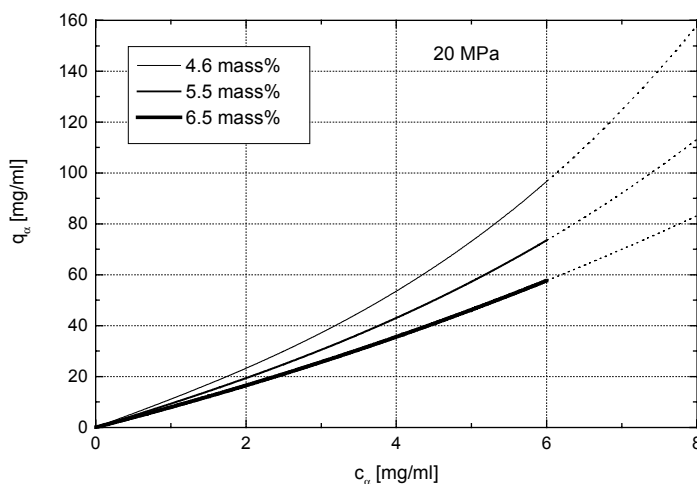


Figure 5:
Influence of modifier concentration on α -tocopherol isotherms on Kromasil KR60-10SIL with CO_2 /2-propanol at $T=313$ K and $P=20$ MPa

Mixture adsorption

The applicability of the IAS theory to the system α -tocopherol/ δ -tocopherol was shown before [2]. In this work isotherms were predicted from single component equilibrium data for different concentration ratios of both tocopherols and for different modifier concentrations. Predicted mixture isotherms of α -tocopherol in mixtures with constant concentration ratios of α - and δ -tocopherol can be seen in Figure 6. The maximal range which is related to experimental data is confined by marker points. As expected for anti-Langmuir adsorption behavior, the adsorption of one component is enhancing the adsorption for the other component.

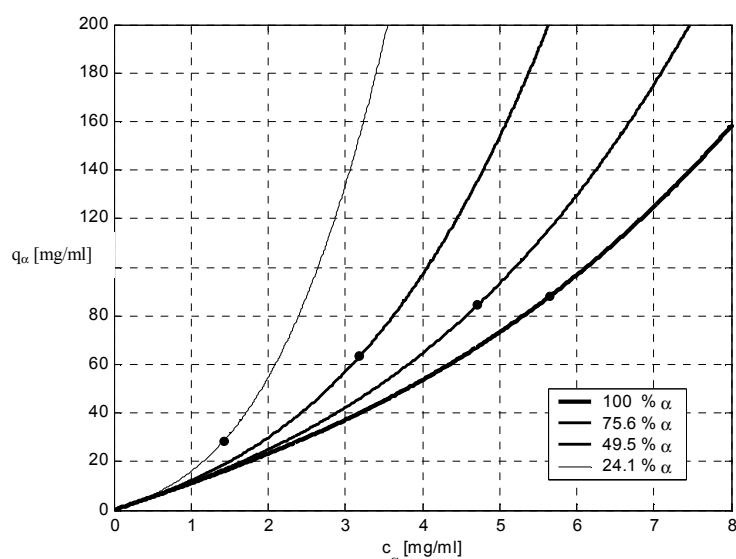


Figure 6:
Mixture isotherms of α -tocopherol on Kromasil KR60-10SIL with CO_2 /4.6 mass% 2-propanol at $P=20$ MPa and $T=313$ K

CONCLUSION

The focus of this research was to acquire adsorption data for α -tocopherol, δ -tocopherol, and β -carotene. The experimental set-up used for these measurements, allows for fast and reliable chromatographic perturbation experiments as well as for chromatographic analysis of injected samples. Using this set-up, adsorption behavior of other mixtures from supercritical solutions can be analysed fast and reliable.

Experiments were successfully performed for both tocopherols at different conditions. In the experiments, fluid phase concentrations of up to $9 \text{ mg}_{\text{tocopherol}}/\text{ml}$ were reached. Fitting parameters of a cubic Hill isotherm to the experimental data was successful. Adsorption of α - and δ -tocopherol shows anti-Langmuir behavior with increasing isotherm slope at higher concentrations. Adsorbent loadings decrease at higher pressures and increasing modifier concentration, which can be explained by higher density and solvent strength of the fluid phase. Data from this work can be used for design and simulation of adsorptive separation processes.

Due to the high solubility of β -carotene in propane, the adsorbent loading was low and isotherms were linear. Following this work, studies should be done on a wider range of concentrations of β -carotene in order to determine the complete adsorption equilibria. Other static methods and dynamic methods could be applied for measurement of adsorption isotherms at higher concentrations. Other adsorbent, such as Tonsil can be used, since it shows much higher loading for carotenoids than silica gel [9].

ACKNOWLEDGEMENT

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