Adsorption of Organics on MSC5A in Supercritical CO_2: Chromatographic Measurements & Stop & Go Simulation

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Abstract: Chromatographic measurements were made for the adsorption of benzene, toluene and m-xylene on molecular sieving carbon (MSC) in a supercritical fluid CO_2 mixed with organics. A supercritical chromatograph packed with MSC was used to detect pulse responses of the organics. Adsorption equilibria and adsorption dynamic parameters for organics were obtained by moment analysis of the response peaks. Dependences of adsorption equilibrium constants, K^*, and micropore diffusivity, D, on the amount adsorbed were examined. The dependencies of adsorption equilibrium constants, K^*, and micropore diffusivities, D, for benzene, toluene and m-xylene, on the molarity of benzene over a range of temperature and pressure were obtained. Experimental results were simulated using the “Stop & Go” method as well as by molecular simulation.

Keywords: *Supercritical fluid chromatography, Stop & go simulation, MSC5A*

1 Introduction

Supercritical CO_2 fluid is an attractive solvent whose solubility for organics can be altered by changes of pressure and temperature. New processes of adsorptive separation using supercritical fluid might be possible since removal of the adsorbate from the adsorbent can be performed efficiently [1].

In this study, chromatographic measurements were made for the adsorption of benzene, toluene and m-xylene on molecular sieving carbon (MSC) in supercritical fluid CO_2. A supercritical chromatograph packed with MSC was used to measure the pulse response of the organics. Adsorption equilibria and adsorption dynamics were obtained by moment analysis of the response peaks. Dependences of adsorption equilibrium constants, K^*, and micropore diffusivity, D, on the amount adsorbed were examined. A “stop & go” simulation of multicomponent adsorption equilibria was performed in order to establish the equilibrium and rate parameters, which were determined by comparing the “stop & go” simulation with the experimental results. Also, potential parameters for the molecular simulation were determined by comparing the molecular simulation with the experimental results and the “stop & go” simulation in the last parts of this paper.

2 Experimental

The experimental apparatus (Super 200-type 3; Japan Spectroscopic Co., LTD) is shown in Fig.1. The carrier fluid for the chromatograph was supercritical CO_2 (critical temperature 304 K, critical pressure 7.3 MPa) and its mixture with the above-stated organics (benzene, toluene or m-xylene) respectively. The adsorbates (used in the form of pulses) were either the same species or another organic mixed with supercritical CO_2.

For example, in the case of CO_2 mixed with benzene, the organic used in the form of pulse was benzene, toluene or m-xylene. The volumes of the pulse were fixed to be 4 x 10^{-9} m^3 as liquid.

MSC 5A (Takeda chemicals Co., HGK882.) was crushed and screened to obtain particle size between 1.49 x 10^{-4} - 1.77 x 10^{-4} m (an average particle radius of 8.12 x 10^{-5} m). 4.82 x 10^{-4} kg of these particles were packed into the chromatographic column of 15 x 10^{-2} m long and 4.6 x 10^{-3} m in diameter. The void fraction, ε, of the bed was determined to be 0.3256. The flow rate of supercritical CO_2 was 1.33 x 10^{-7} m^3/s at 268 K and at 15.0, 20.0 and 25.0 MPa respectively and the flow rate of adsorbate (benzene, toluene or m-xylene) was 1.67 x 10^{-10} m^3/s, 5.00 x 10-10 m^3/s and 1.00 x 10^{-9} m^3/s as liquid at room temperature (298 K). The column pressure was kept at 15.0, 20.0 and 25.0 MPa respectively. The pressure drop across the adsorbent bed was estimated to be about 0.1 MPa and was assumed to be negligible. The experimental column temperature was kept at 313, 333 and 353 K respectively. Before the start of the experimental runs the adsorbent particles were regenerated and stabilized by feeding pure CO_2 for 2 hours at the experimental pressure and temperature. Pulse responses were detected using a multi-wave length UV detector (Multi-340; Japan Spectroscopic Co., LTD.) (195-350 nm). Response data were processed by a personal computer. Moments analysis of the supercritical fluid chromatograms was tried, and the apparent adsorption equilibrium constant, K^* and time constant of micropore diffusivity, D/a^2 were estimated from the first and second moments of the response peak, as in reference [2].

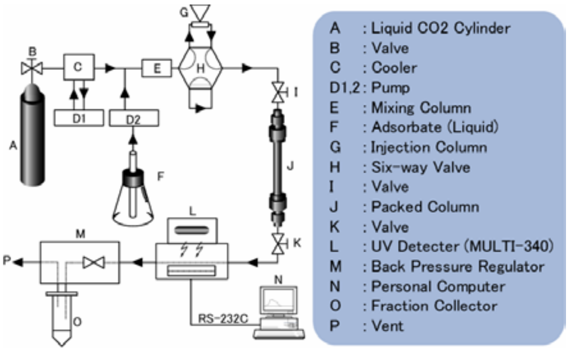

Figure 1: Experimental setup

3 Results and Discussion

3.1 Moments Analysis

Single pulse data were first analyzed for benzene adsorption by the moments method. CO^2 adsorption was considered as background. Later in the Stop & Go simulation, pulse responses were simulated as binary or ternary components. Figure 2 shows the dependency of apparent adsorption equilibrium constants, K*, for benzene, toluene and m-xylene on the amount of benzene adsorbed at 20 MPa, which was estimated from the first moments of the pulses. In the cases of toluene and m-xylene, CO_2 plus benzene adsorption was considered as background. The K^* value for benzene decreases with loading (see Fig. 2). By integrating the benzene data, apparent adsorption isotherms were obtained as shown in Fig. 3.

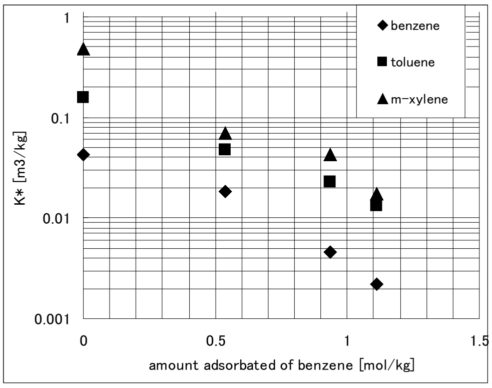

Figure 2: Dependency of apparent adsorption equilibrium constants, K^*, on the amount of adsorbed benzene.

Figure 3 shows apparent adsorption isotherm of benzene at 333 K. According to Fig. 3, the amount adsorbed increases with increasing molarity of benzene, eventually approaching saturation. The amounts adsorbed became larger with decreasing column pressure. This appears to be due to competitive adsorption. The amount of benzene adsorbed decreases as CO_2 adsorption increases with increasing column pressure.

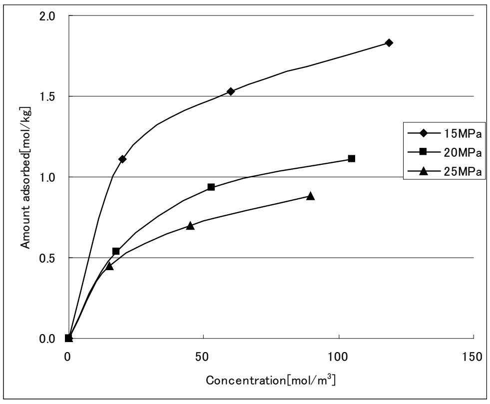

Figure 3: Apparent adsorption isotherm of benzene at 333 K

Figure 4 shows the dependency of micropore diffusivity, $D/\bar{a}^2\exp(\sigma^2)$, for benzene, toluene and m-xylene on the amount of benzene adsorbed at 25 MPa, as obtained from the second moments of the pulses. The increase of $D/\bar{a}^2\exp(\sigma^2)$ for benzene could be reasonably explained by chemical potential driving force. However, the explanation for the dependency of $D/\bar{a}^2\exp(\sigma^2)$ values for toluene and m-xylene on the amount of benzene adsorbed requires further consideration.

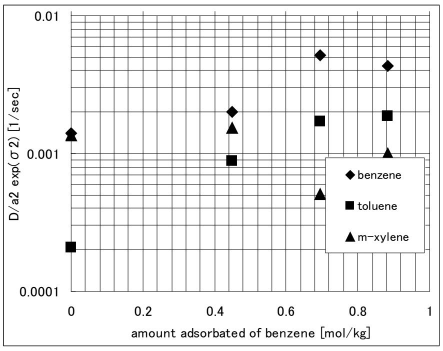

Figure 4: Dependencies of D/a^2 $\exp(\sigma^2)$ on the amount of adsorbed benzene

3.2 Stop & Go Simulation

There are few reported applications of the “Stop & Go” method to simulate perturbation chromatography for the investigation of adsorption kinetics and equilibria. Numerical solution of a multi-component chromatogram in the time domain can be accomplished by using appropriate model equations. This simulated chromatogram can then be compared with the experimental chromatogram to determine the adsorption equilibrium and rate parameters.

Benzene and CO_2 were used as adsorbates. Conditions were 313 K and 15 MPa. The amount of adsorption increased with increasing molarity of benzene. Figure 5-2 shows a comparison of the adsorption isotherm for a stop & go simulation and an experiment.

The co-adsorption isotherm for CO_2 + benzene (Fig. 5-2) was determined by comparisons like that shown in Fig. 5-1. The co-adsorption isotherm for CO_2 + benzene + m-xylene was determined in order to simulate the response shown in Fig. 5-3. The width of the simulated pulse could be adjusted by rate parameter adjustment, but only minor adjustments were required.

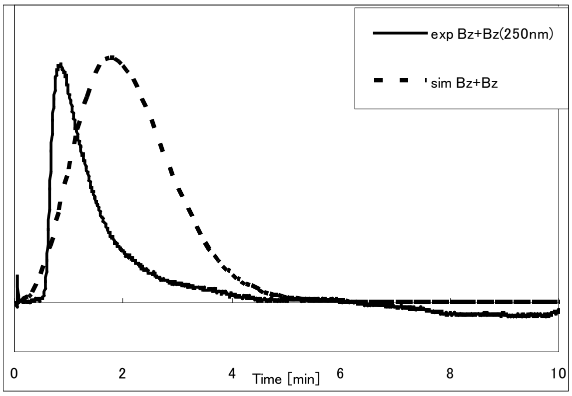

Figure 5-1: Comparison between experimental and simulated pulse response (carrier: CO_2 + benzene, pulse: benzene, 150 atm, 313 K, 0.03 ml/min benzene)

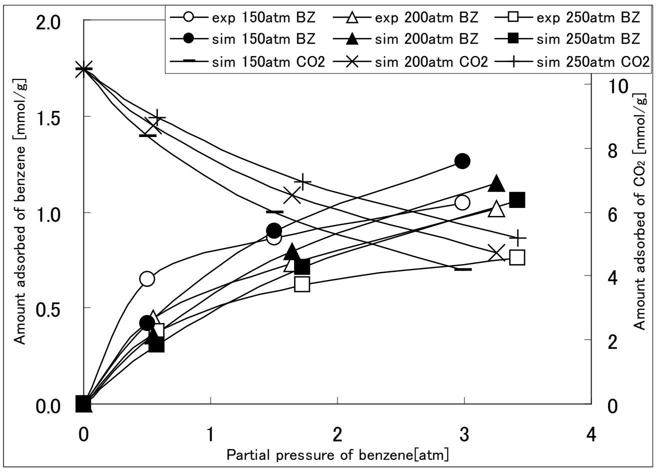

Figure 5-2: Comparison between experimental and simulated adsorption isotherm (carrier: CO_2 + benzene, pulse: benzene, 150 atm, 313 K, 0.03 ml/min benzene)

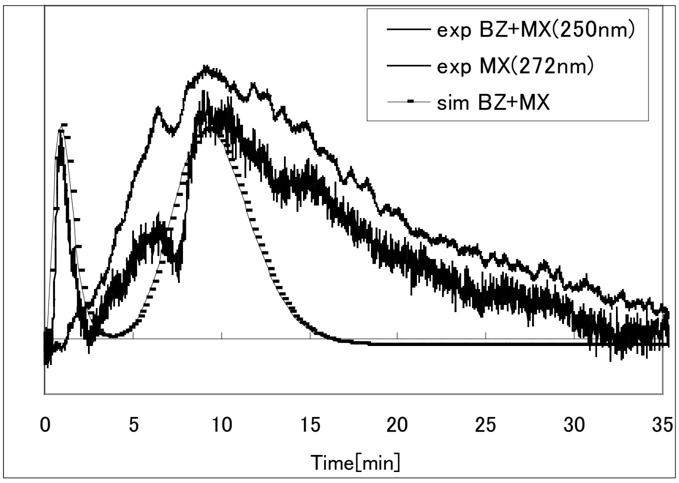

Figure 5-3: Comparison between experimental and simulated pulse response (carrier: CO_2 + benzene, pulse: m-xylene, 150 atm, 353 K, 0.03 ml/min benzene)

Molecular simulation

Cerius2 (MSI Inc.) software was used throughout the simulations. Three kinds of force field parameters in the Cerius2 library were used. The Grand Canonical Monte Carlo method (under constant chemical potential, volume (*V*), and temperature (*T*)) was used to estimate the equilibrium amount adsorbed. The purpose of performing these simulations was to elucidate the adsorption mechanism at the molecular level. The simulation was performed under the same conditions as the experiment in order to allow direct comparison. MSC68-test004 model was used as the adsorbent. The model has 6.8 A of distance between the centers of adjacent graphitic carbon layers.

Adsorption state

First, we examined how adsorbate molecules are located. Benzene was used for the adsorbate. The results are shown in Figure 6. We see from Figure 6 that benzene adsorbs into the adsorption space, which simulates the micropore. Here, benzene adsorbed in parallel to the layers in the MSC68-test004 model.

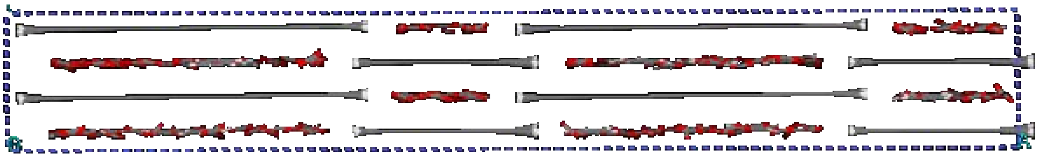

Figure 6: Adsorption state of benzene (MSC68-test004 model)

Adsorption isotherm

The simulation was also carried out for the binary mixtures. With benzene, toluene, m-xylene and CO_2 as the adsorbates. Conditions were 313 K and 15 MPa. The amount of adsorption increased with increasing molarity of benzene, toluene, and m-xylene, respectively. UNIVERSAL1.02 was used for the force field. Figure 7 shows a comparison of the adsorption isotherms from molecular simulation, experiment and Stop & Go simulations, which are almost coincident.

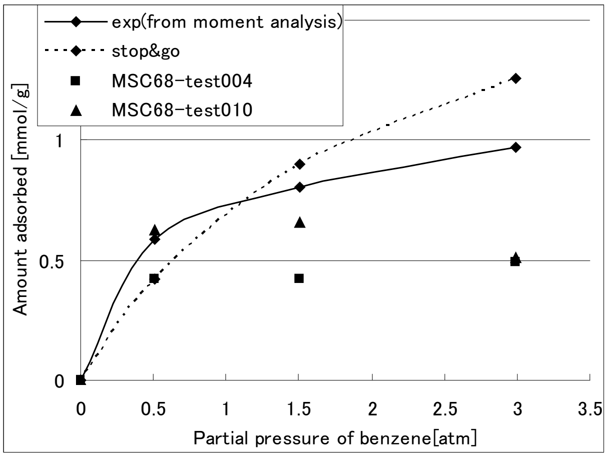

Figure 7: Comparison of experiment, Stop & Go simulation and molecular simulation: Adsorption isotherm (carrier: CO_2 + benzene, pulse: benzene, 150 atm, 313 K)

4. Conclusion

Adsorption equilibrium and adsorption dynamics on MSC were determined by chromatographic measurements for aromatics in supercritical CO_2 mixed with the adsorbate. The dependencies of apparent adsorption equilibrium constants, *K**, and micropore diffusivity, *D*, for benzene, toluene and m-xylene, on molarity of benzene, toluene or m-xylene with temperature and pressure were obtained.. It was found that the values of *K** and *D* for an organic substance depend strongly on the amounts of other organics adsorbed. In the stop & go simulation and molecular simulations, the experimental amount adsorbed could be predicted almost quantitatively. The experimental rate data could be almost replicated by stop & go simulation.

References

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[2] K. Chihara, M. Suzuki, K. Kawazoe, *AIChE Journal 24, 2* (*1978*) *237–246*.

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