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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 supercritical fluid CO_2 mixed with organics. Supercritical chromatograph packed with MSC was used to detect pulse responses of organics. Adsorption equilibria and adsorption dynamics 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 diffusivity, D, of benzene, toluene and m-xylene, on molarity of benzene with each parameters of temperature or pressure were obtained. It was found that the values of K^* and D for an organic substance depended on the amount adsorbed of other organics strongly. And stop & go method was used as simulation method of perturbation chromatography for investigating adsorption equilibrium and rate. Numerical solution for multicomponent chromatogram in time domain could be obtained by appropriate model equations with experimental conditions. This simulated chromatogram can be compared with experimental chromatogram to determine the adsorption equilibrium and rate parameters. In addition, molecular simulation of multicomponent adsorption equilibria was performed, and potential parameters were determined by comparing the simulation with experimental results. Simulation soft ware is Cerius2 (Version 4.2) made by MSI. The purpose of performing simulation is to elucidate an adsorption mechanism on the molecule level.

Keywords Supercritical fluid · MSC · Adsorption · BTX · Chromatography · Moment analysis

1 Introduction

Adsorption of organics on adsorbents, such as activated carbon, in supercritical CO_2 could be mild (Shojibara et al. 1995; Chihara et al. 1997, 2011) compared with adsorption in gas phase (Benkhedda et al. 2000). This is because of co-adsorption of CO_2 (Tanida et al. 1996). Amount adsorbed of organics can be changed by changing temperature and pressure of supercritical CO_2. Adsorption and desorption of organics could be easy and mild in supercritical CO_2 condition. New process of adsorptive separation using supercritical fluid might be possible (Sato et al. 1998). However equilibria and dynamics for co-adsorption of organics and CO_2 have not been studied so much.

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. Supercritical chromatograph packed with MSC was used to detect pulse responses of organics. Adsorption equilibria and adsorption dynamics 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. And, stop & go simulation of multicomponent adsorption equilibria was performed to get reasonable equilibrium parameters and rate parameters. Potential parameters were determined by comparing the molecular simulation with experimental results.

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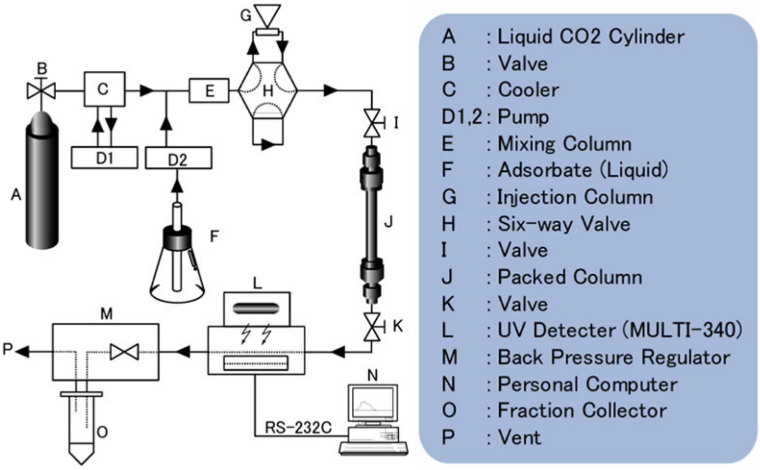


Fig. 1 Experimental setup

2 Experimental

The experimental apparatus (Super 200-type 3; Japan Spectroscopic Co., LTD) was shown in Fig. 1. The carrier fluid of the chromatograph was supercritical CO_2 (critical temperature 304 K, critical pressure 73 atm) and it's mixture with the above-stated organics (benzene, toluene or m-xylene) respectively. The adsorbates used in the form of pulse were the same of or the different from organics 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 4×10^{-9} m^3 as liquid. MSC 5A (Takeda chemicals Co., HGK882) was crushed and screened to obtain particle size between 1.49×10^{-4}–1.77×10^{-4} m (an average particle radius of 8.12×10^{-5} m). 4.82×10^{-4} kg of these particles were packed into the chromatographic column of 15×10^{-2} m long and 4.6×10^{-3} m in diameter. The void fraction, ε, of the bed was determined to be 0.3256. Flow rate of supercritical CO_2 was 1.33×10^{-7} m^3/s at 268 K and at 150, 200 and 250 atm respectively and flow rate of adsorbate (benzene, toluene or m-xylene) was 1.67×10^{-10}, 5.00×10^{-10} and 1.00×10^{-9} m^3/s as liquid at room temperature (298 K).

The column pressure was kept at 150, 200 and 250 atm 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 experimental runs started, 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. Moment analysis of supercritical fluid chromatogram was tried, and the apparent adsorption equilibrium constant, K^* and time constant of micropore diffusivity, D/a^2 obtained from first and second moment of response peak, as in Chihara et al. (1978). Table 1 showed properties of MSC 5A (Chihara et al. 1978).

Table 1 Properties of MSC5A

True density [g/cm^3]	1.8
Particle density [g/cm^3]	0.90
Macropore volume [cm^3/g carbon]	0.38
Micropore volume [cm^3/g carbon]	0.18
Porosity of macropore [−]	0.342
Macropore radius [μ]	2.0
Micropore opening [Å]	5.0

3 Results and discussion

3.1 Moment analysis

Single pulse data were first analyzed for benzene adsorption by moment method. Here, CO_2 adsorption was supposed to be as back ground. Later in stop & go simulation, pulse responses were simulated as binary or ternary components. Figure 2 shows dependency of apparent adsorption equilibrium constants, K^*, for benzene, toluene and m-xylene on the amount adsorbed of benzene at 200 atm, which were obtained from first moments of the pulses. In case of toluene and m-xylene CO_2 plus benzene adsorption was supposed to be as back ground. The K^* of benzene is reasonably decreasing, which corresponds to Fig. 3. By integrating the benzene data, apparent adsorption isotherms were obtained as in Fig. 3.

Figure 3 shows apparent adsorption isotherm of benzene at 333 K. According to Fig. 3, the amount adsorbed increased with increases of molarity of benzene. The amounts adsorbed became larger with decreases of column pressure.

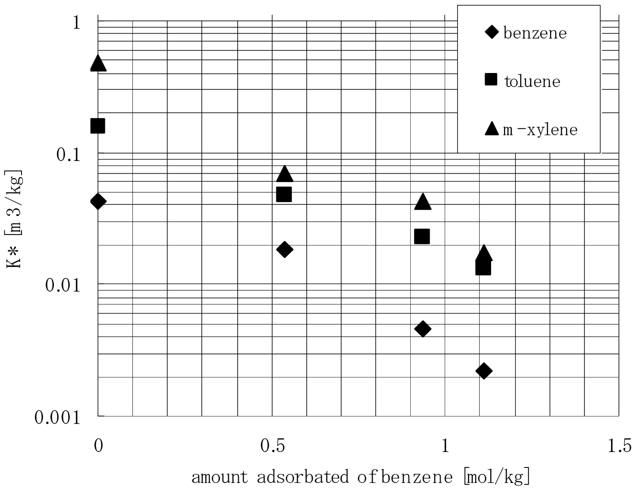


Fig. 2 Dependencies of K^* on the amount adsorbed of benzene

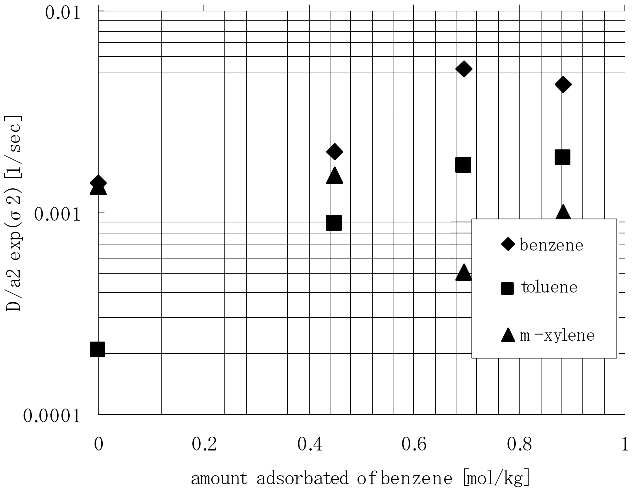


Fig. 4 Dependencies of $D/a^2 \exp(\sigma^2)$ on the amount adsorbed of benzene

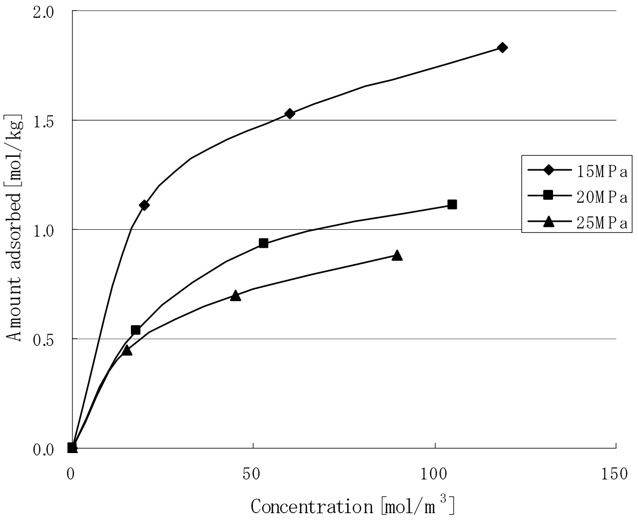


Fig. 3 Apparent adsorption isotherm: benzene at 333 K

It was considered that the situation is competitive adsorption and the amount adsorbed of benzene decreases as CO_2 adsorption increase with increases of column pressure.

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 250 atm, 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 dependency of $D/\bar{a}^2 \exp(\sigma^2)$ values for toluene and m-xylene on the amount of benzene adsorbed requires further consideration.

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. This simulated system (cell model) has the inherent dispersion (mixing between cells), however we can neglect since it has too small effect. Benzene and CO_2 were used for adsorbates. Conditions were 313 K and 150 atm. The amount of adsorption increased with increasing molarity of benzene. Figure 5(a) showed comparison of experimental and simulated pulse responses of each flow rate of benzene in a mixed carrier. Good coincidence of peaks between experiment and simulation were observed as for peak retention and width. The simulated widths were adjusted. We can see the noise (0.06 ml), but it is no problem.

Figure 5(c) 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(c)) was determined by comparisons like that shown in Fig. 5(a) and (b).

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

3.3 Molecular simulation

Cerius2 (MSI Inc.) was used throughout the simulations. Two 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 get the equilibrium amount adsorbed. The purpose of performing simulation is to elucidate an adsorption mechanism on the molecule level. The simulation

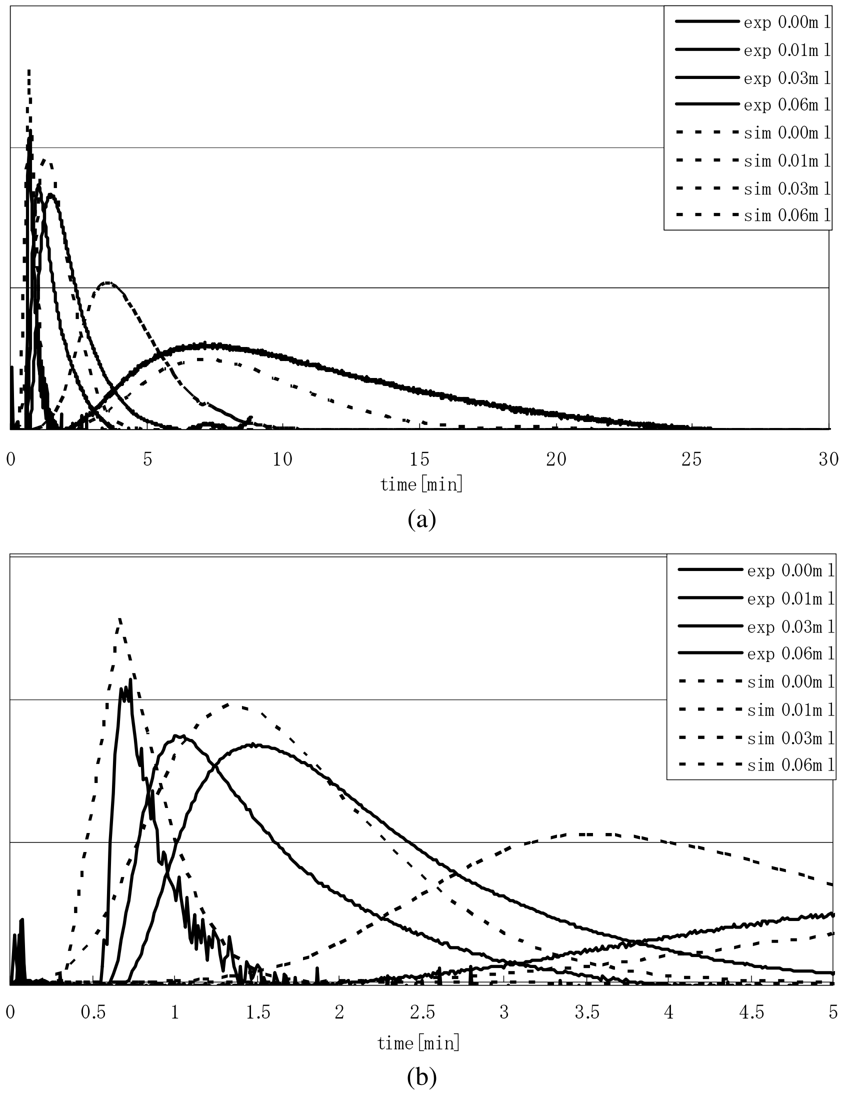


Fig. 5 (**a**) Comparison of experimental and simulated pulse responses of each flow rate of benzene in a mixed carrier in 150 atm and 313 K. (**b**) Comparison of experimental and simulated pulse responses of each flow rate of benzene in a mixed carrier in 150 atm and 313 K (*horizontal axis* is expanded from (**a**). (**c**) Comparison between experimental and simulated adsorption isotherm (carrier: $CO_2 +$ benzene, pulse: benzene, 150 atm, 313 K, 0.03 ml/min benzene). (**d**) Comparison between experimental and simulated pulse response (carrier: $CO_2 +$ benzene, pulse: m-xylene, 150 atm, 353 K, 0.03 ml/min benzene)

was performed on the same conditions as an experiment in order to compare with experiments. MSC68-test004 model was used as adsorbent. The model has 6.8 A of distance between the centers of two graphitic carbon layers.

3.4 Adsorption state

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

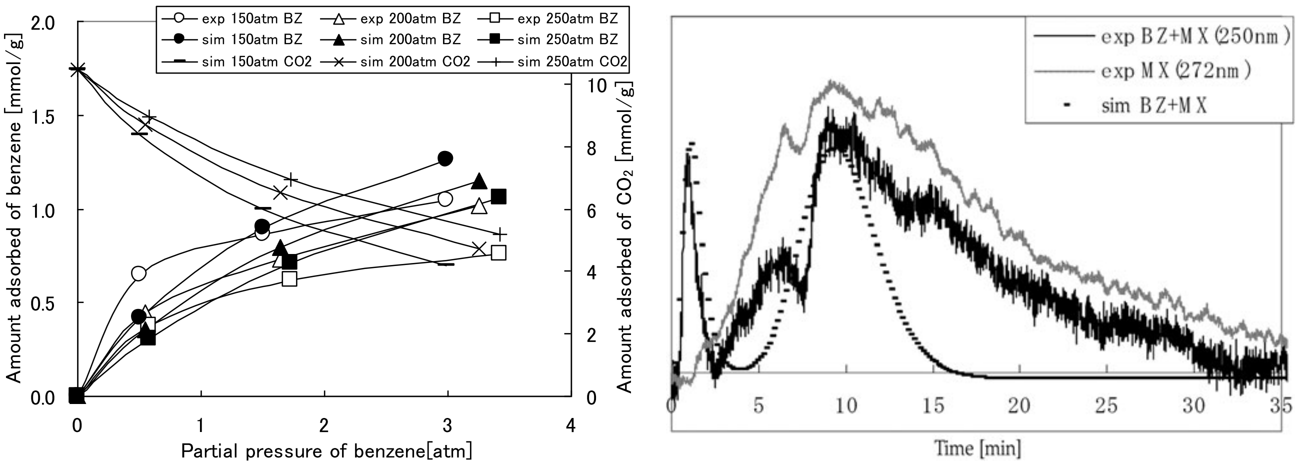
3.5 Adsorption isotherm

The simulation was carried out for the binary component. Benzene and CO_2 were used for adsorbate. Conditions were 313 K and 150 atm. The amount adsorbed increased with increases of molarity of benzene. The amount adsorbed of CO_2 decreased with increases of molarity of benzene. UNIVERSAL1.02 and DREIDING2.11 was used for the force field. Figure 7 shows comparison of adsorption isotherms for molecular simulation, and experiment to get almost coincidence.

Right hand figure was revised as for the length of the graphite layer in Fig. 6. Benzene amount adsorbed increased slightly.

4 Conclusion

Adsorption equilibrium and adsorption dynamics on MSC were evaluated for each organics in supercritical CO_2 fluid mixed with adsorbate by chromatographic measurement. The dependencies of apparent adsorption equilibrium constants, K^*, and micropore diffusivity, D, of benzene, toluene



(c) (d)

Fig. 5 (*Continued*)

Fig. 6 Adsorption state of benzene (MSC68-test004 model)

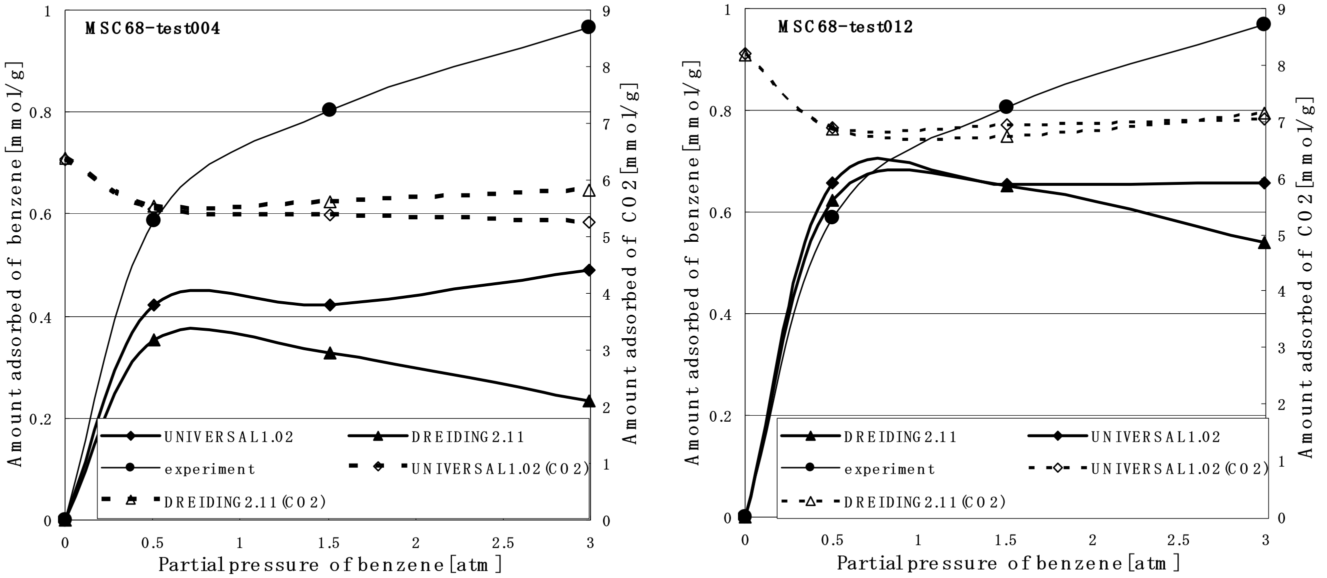


Fig. 7 Comparison with experiment and molecular simulation: adsorption isotherm (carrier: CO_2 + benzene, pulse: benzene, 150 atm, 313 K)

and m-xylene, on molarity of benzene, toluene or m-xylene with each parameters of temperature or pressure were obtained, respectively. It was found that the values of K^* and D for an organic substance depended on the amount adsorbed of other organics strongly. In the simulation, stop & go simulation and molecular simulation, the experimental amount adsorbed could be almost simulated. And the experimental rate could be almost simulated by stop & go simulation.

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