Adsorption of Organics on MSC5A in Supercritical CO2, Molecular 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 CO2 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 toluene, benzene and m-xylene, on molarity of toluene 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, 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 (Version4.2) made by MSI. The purpose of performing simulation is to elucidate an adsorption mechanism on the molecule level. As for the amount adsorbed, especially in DREIDING2.11, the simulation shows the value near experiment.

Keywords

adsorption, supercritical fluids, molecular simulation, moment analysis

1. INTRODUCTION

Supercritical CO2 fluid is attractive solvent whose solubility of organics can be changed with changes of pressure and temperature. New process of adsorptive separation using supercritical fluid might be possible since removal of adsorbate from adsorbent can be performed efficiently.

In this study, chromatographic measurements were made for the adsorption of benzene, toluene and m-xylene on molecular sieving carbon (MSC) in supercritical fluid CO2. 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, molecular simulation of multicomponent adsorption equilibria was performed, and potential parameters were determined by comparing the simulation with experimental results.

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 CO2 (critical temperature 304K, critical pressure 7.3 MPa) 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 CO2.

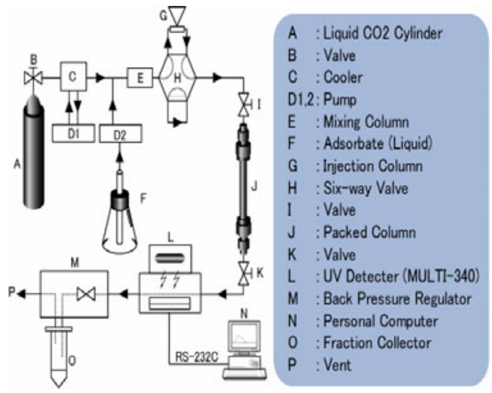


Table 1. Example of a Sample Table and the Table Caption

For example, in the case of CO2 mixed with benzene, the organic used in the form of pulse was benzene or, toluene or m-xylene. The volumes of the pulse were fixed to be 10 x 10-9m3 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. 10-4m (an average particle radius of 8.12 x. 10-5 m). 4.82 x 10-4kg of these particles were packed into the chromatographic column of 15 x 10-2m long and 4.6 x 10-3m in diameter. The void fraction, ε, of the bed was determined to be 0.3256. Flow rate of supercritical CO2 was 1.33 x 10-7m3/s at 268K and at 15.0, 20.0 and 25.0MPa respectively and flow rate of adsorbate (benzene, toluene or m-xylene) was 1.67 x 10-10m3/s, 5.00 x 10-10 m3/s and 1.00 x 10-9 m3/s as liquid at room temperature (298K). 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 0.1Mpa 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 CO2 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/a2 obtained from first and second moment of response peak, as in references .

3. RESULT AND DISCUSSION

Figure.2 shows adsorption isotherm of benzene at 313K. According to Fig.2, the amount adsorbed increased with increases of molarity of benzene, and reached to saturation. The amounts adsorbed became larger with decreases of column pressure. It was considered that the situation is competitive adsorption and amount adsorbed of benzene decreases as CO2 adsorption increase with increases of column pressure.

Figure.3 shows dependency of adsorption equilibrium constants, K*, for benzene, toluene, and m-xylene on amount adsorbed of benzene at 20Mpa. This is reasonably decreasing, which corresponds to Figure.2

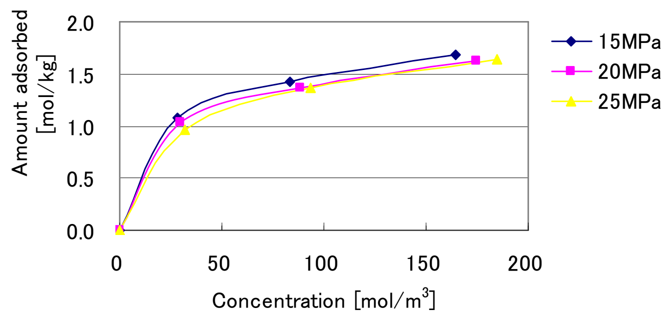


Figure.2 Adsorption isothem : benzene at 313K

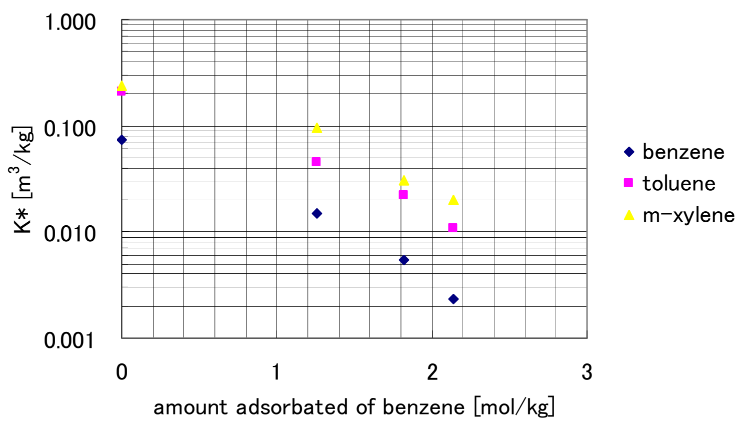


Figure.3 Dependencies of K* on the amount adsorbed of benzene

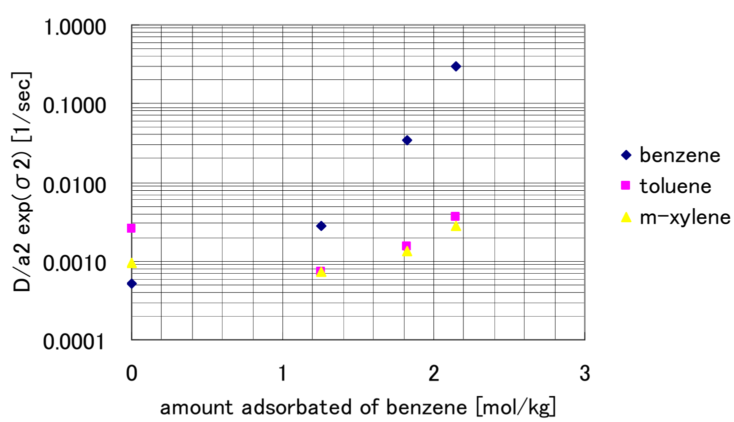


Figure.4 Dependencies of D/a2 exp(σ2) on the amount adsorbed of benzene

Figure.4 shows dependency of micropore diffusivity, D/ā2exp(σ2), for benzene, toluene, and m-xylene on amount adsorbed of benzene at 20MPa. The increase of D/ā2exp(σ2) for benzene could be reasonably explained by chemical potential driving force. However, as for dependency of D/ā2exp(σ2) of toluene and m-xylene on amount adsorbed of benzene, further discussion would be necessary.

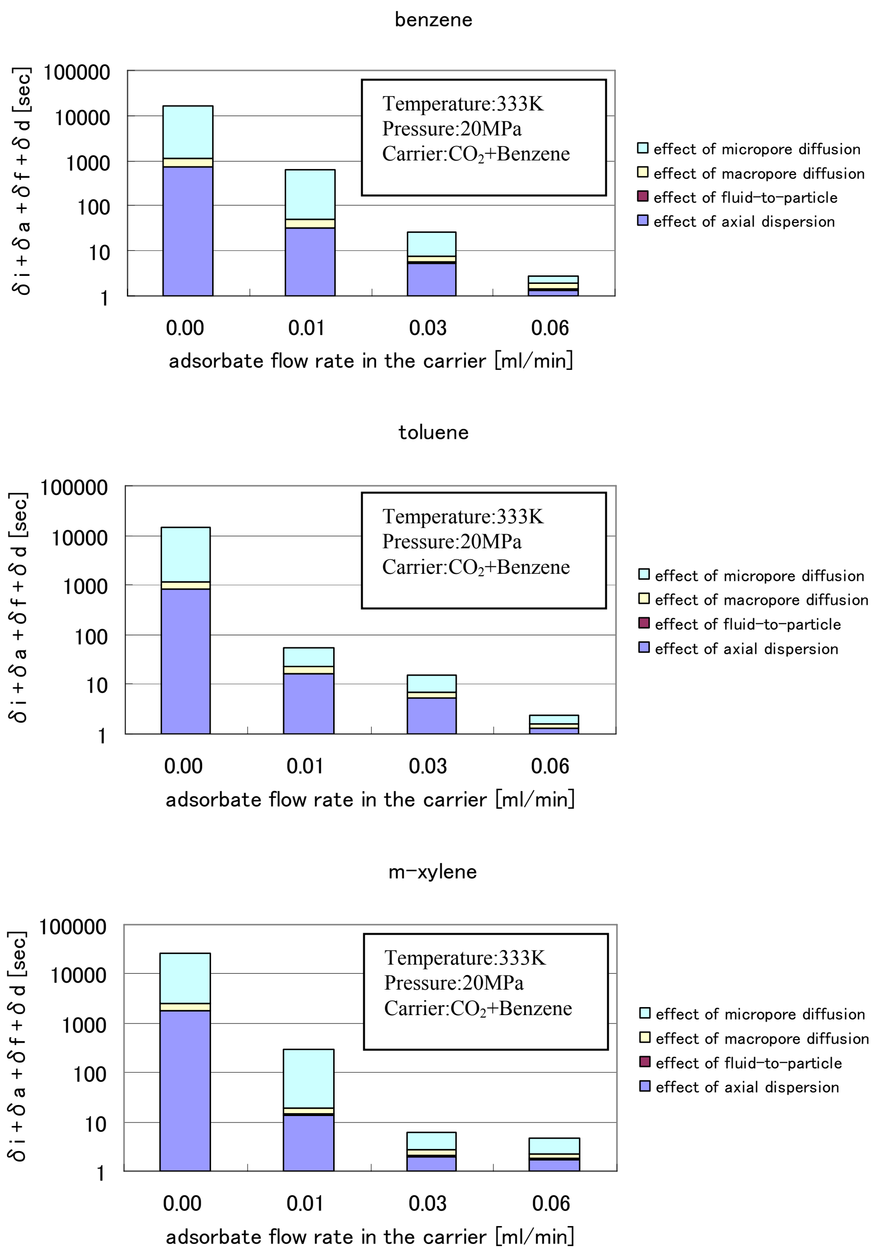


Figure.5 Contribution of four mass transfer steps

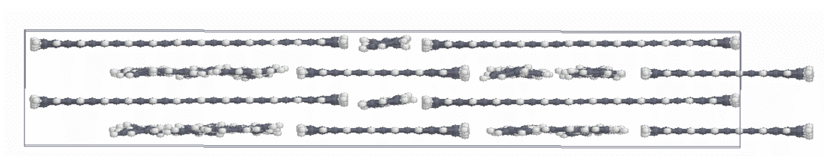
Figure.5 shows contribution of four mass transfer steps in pulse response (□’2). The effect of micropore diffusion is dominant in all the conditions examined.

4. MOLECULAR SIMULATION

Cerius2 (MSI Inc.) was used throughout the simulations. Three kinds of forcefield parameters in the Cerius2 library were used. The Grand Caronical Monte Carlo method (under constant chemical potential (□), volume (V), 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 was performed on the same conditions as an experiment in order to compare with experiments. MSC68-RC1 model was used as adsorbent. The model has 6.8A of distance between the centers of two graphitic carbon layers.

4.1 Adsorption state

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

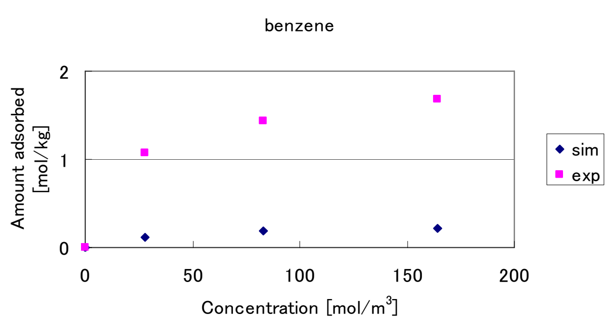


MSC 68RC1 model

Figure.6 Adsorption state of benzene

4.2 Adsorption isotherm

The simulation was carried out for the binary component. Benzene and CO_2 were used for adsorbate. Conditions are 313K and 150atm. The amount of adsorption increased with increases of molarity of benzene. Figure 7 shows comparison of adsorption isotherm for a molecular simulation and an experiment.



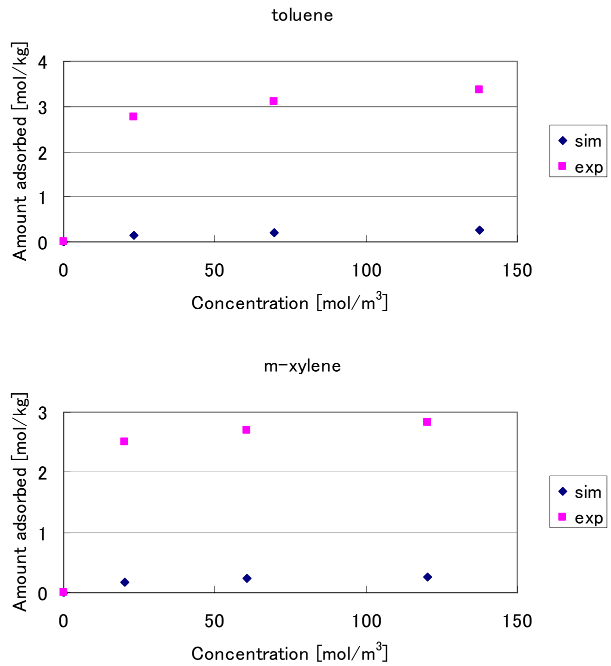


Figure 7. Comparison with experiment and molecular simulation : Adsorption isothermn

Figure 7.shows comparison of the adsorption isotherm of simulations and experiments. MSC68-RC1 was used for the adsorbent model and the simulation was carried out with CO2 and ingredient carried using benzene or toluene or m-xylene. UNIVERSAL1.02 was used for the force field parameter. There are the big difference between the simulation result and the experimental result in the amount of adsorption. It was found that the simulation result dropped to about 1/10. More improvement for simulation would be necessary.

5. CONCLUSION

Adsorption equilibrium and adsorption dynamics on MSC were evaluated for each organics in supercritical CO2 fluid mixed with adsorbate by chromatographic measurement. The dependencies of adsorption equilibrium constants, K*, and micropore diffusivity, D, of toluene, benzene 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. The usefulness of a simulation was able to be seen by one of the features of the molecule simulation that a molecule can be visuallized, about the adsorption state. The experimental amount adsorbed could not be simulated yet.

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