

## Study of Multi-Component Gas Adsorption by Chromatographic Method and Simulation

*Kazuyuki Chihara, Hidenori Nakamura, Yuki Teramura, Yousuke Kaneko*

Department of Applied Chemistry, Meiji University, 1-1-1 Higashi-mita, Tama-ku,  
Kawasaki, Kanagawa, 214-8571, Japan, E-mail: chihara@isc.meiji.ac.jp

### 1. Introduction

The combination of chromatographic method and moment analysis of the response peaks is one of the useful techniques to study adsorption equilibrium and adsorption rate. Perturbation chromatography with the mixed multi component adsorbate gas carrier (two adsorbates) has been applied to several studies on adsorption. In this work, perturbation chromatography with multi component gas carrier (two adsorbates with inert gas) and non-equilibrium thermodynamics linear law was applied for discussion of the interference effect and the displacement effect (those are cross effects) on mass transfer in multi-component gas adsorption as previous study for different gas mixture (He, N<sub>2</sub>, CH<sub>4</sub>). Moment analysis method and stop & go simulation method were utilized to obtain each mass transfer parameters of adsorbate gases. Dependency of micropore diffusion on amount adsorbed and correlation of micropore diffusion with chemical potential driving force for microporous adsorbent were discussed. Also, cross effects were discussed. Ruthven already pointed out the dependency of micropore diffusivity on amount adsorbed in single component adsorption. Tondeur et al gave general background on multi-component perturbation chromatography for the first moment only.

### 2. Experimental method

The apparatus was similar to a conventional gas chromatograph. Adsorbent particles (molecular sieving carbon 5A, 20/30 mesh, Japan Enviro Chemical Ltd.,) were packed in a column. Carrier gas was a mixture of two or three components among He, CO<sub>2</sub>, CH<sub>4</sub>. Perturbation pulse was introduced into the carrier gas stream. Introduction of pulses was performed by 6-way valve. The pulse size was 1cc, which meant injection period was 1.4 sec. Then pulse response was detected by TCD cell. Output signal of TCD was transmitted to a personal computer through RS232C. This signal was also transmitted to the personal computer. Simulated chromatogram by a personal computer can be overlapped on experimental chromatogram shown in the monitor screen. Further, moment of pulse response, which is shown in the monitor screen, can be automatically calculated by the personal computer.

### 3. Simulation method

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 equilibrium and the adsorption kinetic parameters. Here Markham-Benton equation as for adsorption equilibrium and linear driving force (LDF) approximation as for adsorption

kinetics were adapted for numerical calculation, which was based on stop & go method. In particular, LDF model of adsorption kinetics was based on non-equilibrium thermodynamics. Overall mass transfer coefficients ( $K_{sav}$ ) for LDF model were determined. Then, micropore diffusivities were obtained by subtracting other mass transfer effects from overall resistance ( $g/K_{sav}$ ). Thus obtained micropore diffusivities were correlated with chemical potential driving force by consideration of Fick's diffusion equation and non-equilibrium thermodynamics.

#### 4. Result and Discussion

Fig.1 shows an example of comparison of experimental chromatogram with simulated chromatogram for MSC5A to obtain  $K_{sav}$  for LDF model. Experimental conditions were 313 K, column pressure 5 atm, flow rate 25 cm/sec and He + CH<sub>4</sub> mixed gas carrier with CH<sub>4</sub> pulse. Here CH<sub>4</sub> concentration in the carrier gas was changed 10, 30, 50, 70 and 90 %. Retention time of simulation peak depend on langmuir parameter. Experimental peaks differ from simulation peaks.

Fig.2 shows experiment and simulation results in an example case of binary adsorbate carrier mixed with He and an adsorbate pulse for MSC5A. Experimental conditions were 313 K, column pressure 5 atm, flow rate 25 cm/sec and He(30%)+CO<sub>2</sub>(60%)+CH<sub>4</sub>(10%) mixed gas carrier with CH<sub>4</sub> pulse. Simulation peak needs compensation.

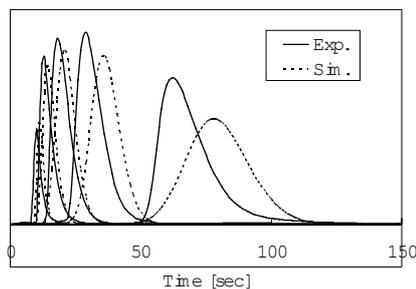


Fig. 1 Comparison of experimental peaks with simulation of He + CH<sub>4</sub> mixed gas carrier with CH<sub>4</sub> pulse at 313 K.

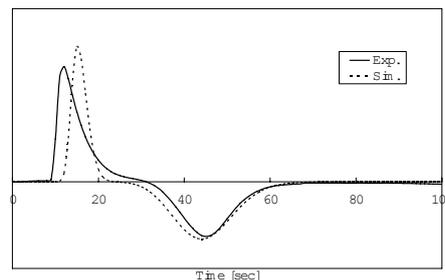


Fig. 2 Comparison of experimental peaks with simulation of He(30%)+CO<sub>2</sub>(60%)+CH<sub>4</sub>(10%) mixed gas carrier with CH<sub>4</sub> pulse at 313 K.

#### 5. Conclusion

Good agreements between experimental chromatogram and simulated chromatogram, which were based on the modeling of Stop & Go method, were observed in case of perturbation chromatography with mixed adsorbate gas carrier. The micropore diffusivities obtained were interpreted by chemical potential driving force consideration based on non-equilibrium thermodynamics.