

CHROMATOGRAPHIC STUDY OF MULTICOMPONENT GAS ADSORPTION ON MSC5A

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Abstract

Perturbation chromatography with multi component gas carrier and non-equilibrium thermodynamics liner law was applied for discussion of the interference effect and the displacement effect on mass transfer in multi component gas adsorption. 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 confirmed. Cross effect in micropore diffusion was found.

Keywords

chromatograph, stop & go simulation, multi component gas

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 (Chihara et al. 1978). Perturbation chromatography with the mixed multi component adsorbate gas carrier (two adsorbates) has been applied to several studies on adsorption (Ruthven and Kumar 1979, Kumar et al. 1982). In this work, perturbation chromatography with multi component gas carrier (two adsorbates with inert gas) and non-equilibrium thermodynamics liner 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. 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 effect were discussed. Ruthven already pointed the dependency of micropore diffusivity on amount adsorbed in single component adsorption (Ruthven 1984). Tondeur et al gave general background on multi component perturbation chromatography for the first moment only (Tondeur 1996).

2. Experimental Method

2.1. Experimental Procedure and Conditions

The experimental apparatus was shown in figure1. 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 (100cm x 3mm i.d.). Carrier gas was a mixture of two or three components among He, N₂, CH₄. 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 and by mass filter (Dycor quadrupole mass detector). Output signal of TCD was transmitted to a personal computer through RS232c. Also, pulse response was

introduced to mass detector to get individual response of each component. These signals were 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.

The first absolute moment and the second central moment were evaluated from the effluent peak $C_e(t)$ as follows:

$$\mu_1 = \int_0^{\infty} C_e(t) t dt / \int_0^{\infty} C_e(t) dt \quad (1) \quad \mu_2' = \int_0^{\infty} C_e(t) (t - \mu_1)^2 dt / \int_0^{\infty} C_e(t) dt \quad (2)$$

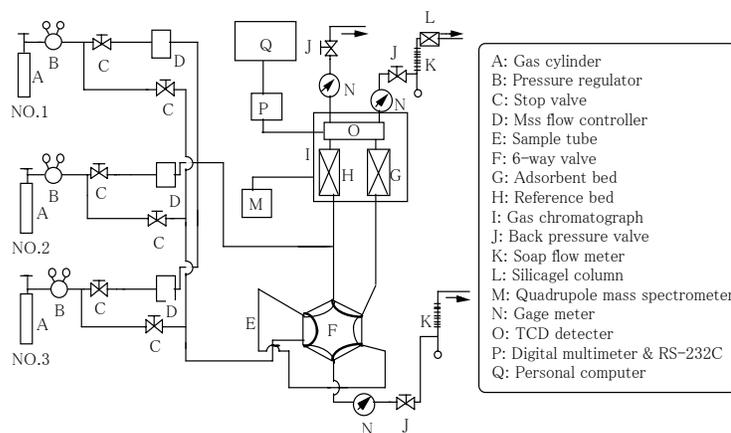


Figure 1. Experimental apparatus

2.2. Moment Analysis

Basic equations are in ref. (Kumar et al. 1982)

The resultant moment equations of the impulse response are

$$\mu_1 = \frac{z}{u} \left\{ 1 + \frac{(1-\varepsilon)\rho_p(1-y)K^*}{\varepsilon} \right\} \quad (3)$$

$$\mu_2 = \frac{2z}{u} \left[Ez \left\{ \frac{1 + (1-\varepsilon)\rho_p K^*}{\varepsilon u} \right\}^2 + \frac{(1-\varepsilon)\rho_p(1-y)K^*}{\varepsilon K_s a v} \right] = \frac{2z}{u} (\delta_d + \delta_f + \delta_a + \delta_i) \quad (4)$$

where μ_1 =first absolute moment of the chromatographic peak[s] μ_2 =second central moment[s²].

$$\delta_d = \frac{Ez}{u^2} \left\{ 1 + \frac{(1-\varepsilon)\rho_p(1-y)K^*}{\varepsilon} \right\}^2 \quad (5)$$

$$\delta_f = \frac{1-\varepsilon}{\varepsilon} \frac{R}{3k_f} \rho_p^2 (1-y) K^{*2} \quad (6)$$

$$\delta_a = \frac{1-\varepsilon}{\varepsilon} \frac{R^2}{15D_a} \rho_p^2 (1-y) K^{*2} \quad (7)$$

$$\delta_i = \frac{1-\varepsilon}{\varepsilon} \frac{\rho_p(1-y)K^*}{15D} a^{-2} \exp(\sigma^2) \quad (8)$$

where K^* =apparent adsorption equilibrium constant, Ez =axial dispersion coefficient based on void spaces in the bed, k_f =external mass transfer coefficient, D_a =diffusivity in macropores and D_i =diffusivity in micropores based on amount adsorbed gradient driving force. The arithmetic average radius \bar{a} is 8.2 μm (Chihara, Suzuki and Kawazoe 1978).

Equation(3) was used along with the experimental μ_1 to obtain the adsorption constant K^* .

Equation(4) to (8) were used along with the experimental μ_2' to obtain the diffusivity in micropores D .

2.3. Stop & Go Simulation

Numerical solution for multi component 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 (Chihara et al. 1986, Chihara and Kondo 1986). In particular, LDF model of adsorption kinetics was based on non-equilibrium thermodynamics.

For binary adsorbates, adsorption rate equations are

$$\gamma \frac{\partial q_1}{\partial t} = K_{sav,1,1}(q_1^* - q_1) + K_{sav,1,2}(q_2^* - q_2) \quad (9) \quad \gamma \frac{\partial q_2}{\partial t} = K_{sav,2,1}(q_1^* - q_1) + K_{sav,2,2}(q_2^* - q_2) \quad (10)$$

where K_{sav} = Overall mass transfer coefficients.

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 (γ/K_{sav}). Thus obtained micropore diffusivities were correlated with chemical potential driving force by consideration of Fick's diffusion equation, non-equilibrium thermodynamics and extended Langmuir equation (Karger and Bulows 1975).

$$\frac{D_{11}}{a^2} = \frac{D_1'}{a^2} \frac{\partial \ln p_1}{\partial \ln q_1} = \frac{D_1'}{a^2} \frac{1 - \theta_2}{1 - \theta_1 - \theta_2} \quad (11)$$

$$\frac{D_{12}}{a^2} = \frac{D_1' q_1}{a^2} \frac{\partial \ln p_1}{\partial \ln q_2} = \frac{D_1'}{a^2} \frac{\theta_1}{1 - \theta_1 - \theta_2} \quad (12)$$

$$\frac{D_{21}}{a^2} = \frac{D_2' q_2}{a^2} \frac{\partial \ln p_2}{\partial \ln q_1} = \frac{D_2'}{a^2} \frac{\theta_2}{1 - \theta_1 - \theta_2} \quad (13)$$

$$\frac{D_{22}}{a^2} = \frac{D_2'}{a^2} \frac{\partial \ln p_2}{\partial \ln q_2} = \frac{D_2'}{a^2} \frac{1 - \theta_1}{1 - \theta_1 - \theta_2} \quad (14)$$

For instance, K_{sav} is related to D in single adsorbate case as

$$\frac{1}{K_{sav}} = \frac{a^2}{15D} + K^* \left(\frac{R}{3k_f} + \frac{R^2}{15\epsilon D_a} \right) \quad (15)$$

For binary case, when using Equation (15), apparent K^* could be determined by appropriate slope of adsorption isothermal plane at perturbation point.

3. Result And Discussion

3.1. Single Adsorbate Carrier Mixed with He and The Same Adsorbate Pulse

Figure 2. 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 5atm, flow rate 25cm/sec and He+CH₄ mixed gas carrier with CH₄ pulse. Here CH₄ concentration in the carrier gas was changed 20,40, 60 and 80 %.

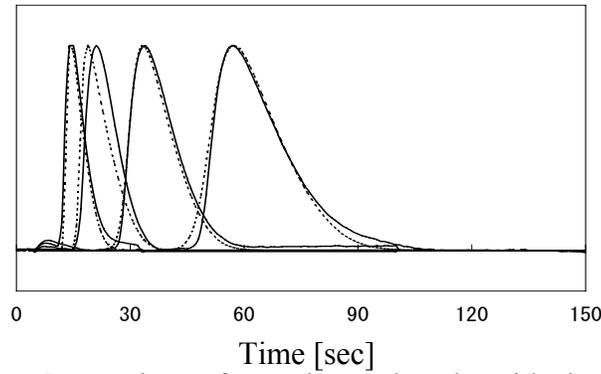


Figure 2. Comparison of experimental peaks with simulation

Figure 3. shows contribution of axial dispersion, external mass transfer, macropore diffusion and micropore diffusion in case of N_2 for MSC5A. This figure illustrated that mass transfer is controlled by micropore diffusion.

Figure 4. shows the dependency of micropore diffusivity coefficient of CH_4 with amount adsorbed at 303, 313 and 323 K for MSC5A.

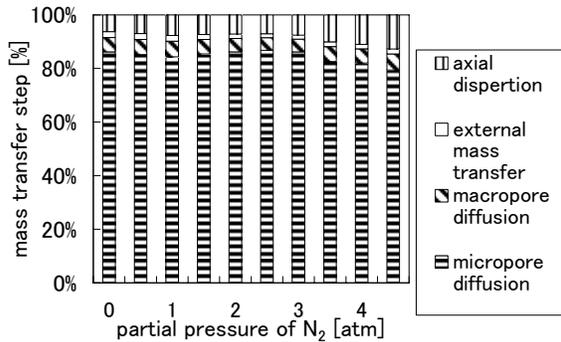


Figure 3. Mass transfer steps of N_2 on to MSC5A

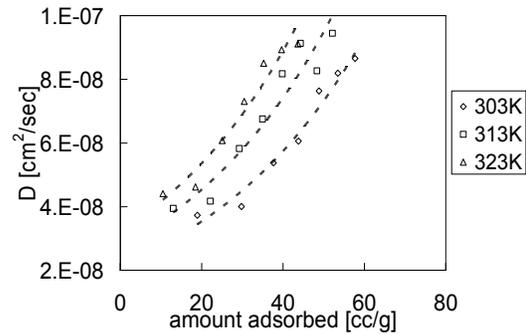


Figure 4. Dependency of micropore diffusivity coefficient on the amount adsorbed

Figure 5. shows the correlation of micropore diffusivity of CH_4 with chemical potential driving force at 303, 313 and 323K for MSC5A. Proportional relation was obtained, which means that micropore diffusion is based on chemical potential driving force.

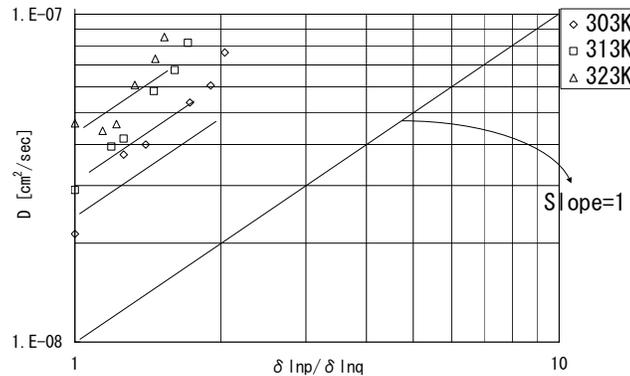


Figure 5. Correlation based on chemical potential driving force

3.2. Binary Adsorbate Carrier Mixed with He and Adsorbate Pulse

Figure 6-(a). to (e) show experimental and simulation results in an example case of binary adsorbate carrier mixed with He and an adsorbate pulse for MSC5A. Experimental conditions were 313K, column pressure 5atm, flow rate 25cm/sec and He(60%)+N₂(10%)+CH₄(30%) mixed gas carrier with N₂ pulse. Figure6-(a) is the comparison between experimental and simulated TCD peaks. Two simulated TCD peaks are those for accounted and not accounted for cross effect. Figure6-(b) is simulated peaks of each gas component and total peak. The total peak is assumed to be the sum of adsorbate peaks except He and assumed to be as simulated TCD peak, which was found to be coincident with experiment as in Figure6-(a). Figure6-(c) to (e) show experimental peaks of the components by mass detector. Each peaks in figure6-(b) could be compared to corresponding peak in figure6-(c) to (e) and to be found in good agreement. Simulated chromatogram for N₂ and CH₄ mixture may be regarded as co-diffusion or competitive adsorption for 1st peak and as counter-diffusion or displacement adsorption for 2nd peak.

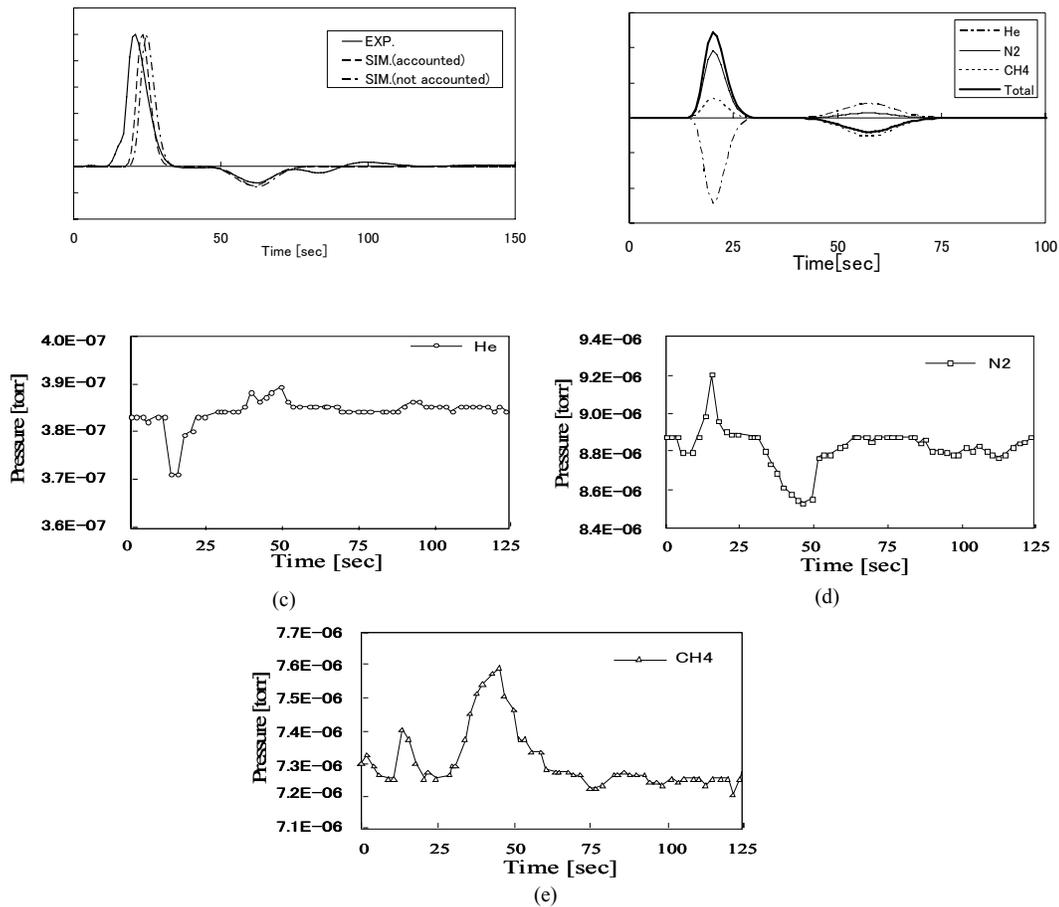


Figure 6. Comparison between experimental chromatogram and simulated one (a), Simulation of pulse response of each component (b), Experimental peak of Helium by mass detector (c), Experimental peak of N₂ by mass detector (d) and Experimental peak of CH₄ by mass detector (e)

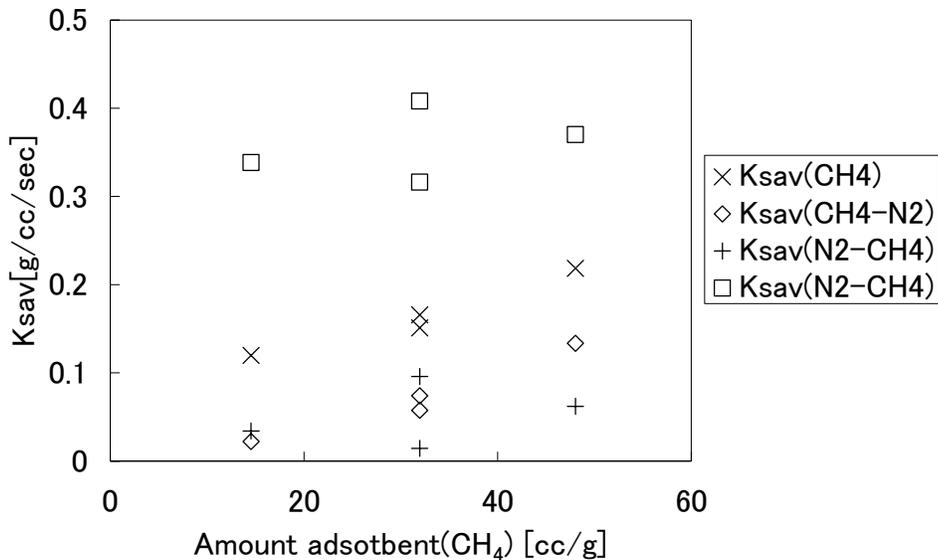


Figure 7. Comparison of K_{sav} of single adsorbate, and K_{sav} of binary adsorbate [He+ CH₄- N₂]

Figure 7. shows K_{sav} obtained by Eq.(11)~(15) neglecting macro effect for binary adsorbates system, corresponding to Figure 6. It was found that K_{sav} obtained by consideration of chemical potential driving force with cross effect was well applied to get good simulation results for multicomponent pulse response.

4. 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. And micropore diffusivities obtained were interpreted by chemical potential driving force consideration based on non-equilibrium thermodynamics law. Some possibility was shown for cross effect of micropore diffusion in multicomponent adsorption.

5. References

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