

Diffusion in Multicomponent Gas Adsorption on MSC5A, Chromatographic study

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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 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. 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 (MSC5A) were packed in a column. 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. 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.

3. 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

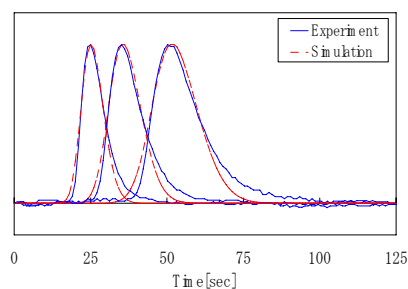


Fig.1: Comparison of experimental peaks with simulation

25[cm/sec] and He+CH₄ mixed gas carrier with CH₄ pulse. Here CH₄ concentration in the carrier gas was changed 40, 60 and 80[%].

Fig.2 shows the dependency of micropore diffusivity coefficient of CH₄ with amount adsorbed at 303, 313 and 323 [K] for MSC5A.

Fig.3 shows the correlation of micropore diffusivity of CH₄ with chemical potential driving force at 303, 313 and 323[K] for MSC5A. Proportional relation was obtained, which means that micropore diffusion is based on chemical potential driving force.

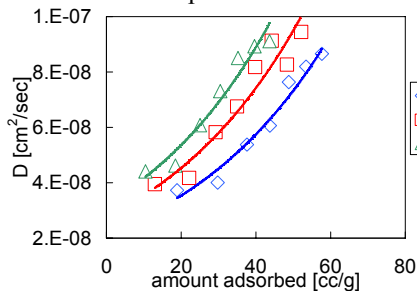


Fig.2: Dependency of micropore diffusivity

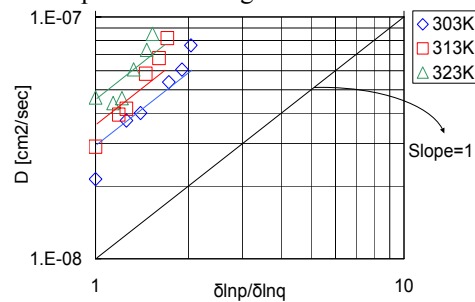


Fig.3: Correlation based on chemical potential driving force

Fig.4 shows comparison of K_{sav} obtained from single adsorbate system and binary adsorbates system. Both K_{sav} for N₂ and CH₄ for single experiment show dependencies on amount adsorbed itself. As for K_{sav} for binary adsorbate [He+CH₄ carrier + N₂ pulse], CH₄-binary shows reasonable dependency, same as single case. Here N₂-binary should remain constant, cause no amount adsorbed in the column. However, the K_{sav} for N₂ is affected by CH₄ adsorption, as if there is some N₂ amount adsorbed.

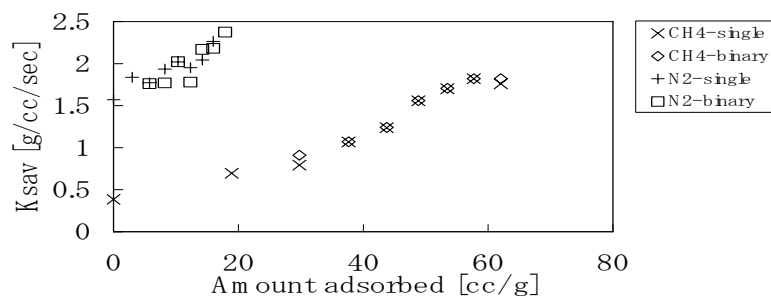


Fig.4: Comparison of K_{sav} of single adsorbate, and K_{sav} of binary adsorbate [He+ CH₄- N₂]

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.

References

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2.2 Moment Analysis

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

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

1st moment was calculable from the retention time of the peak. And 2nd moment was calculable from the retention width.

Equation (3) was used along with the experimented 1st moment to obtain the absorption equilibrium constant K^* .

Equations (4), (5), (6), (7), (8) were used along with the experimented 2nd moment to obtain the diffusivities in the micropore.

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

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

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

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

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

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

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

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

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

where $Ksav$ = Overall mass transfer coefficients.

Overall mass transfer coefficients ($Ksav$) for LDF model were determined. Then, micropore diffusivities were obtained by subtracting other mass transfer effects from overall resistance ($\gamma/Ksav$). Thus obtained micropore diffusivities were correlated with chemical potential driving force by consideration of Fick's diffusion equation and non-equilibrium thermodynamics (Karger and Bulows 1975).

$$\frac{D_{11}}{a^2} = \frac{D_1'}{a^2} \frac{\delta \ln p_1}{\delta \ln q_1} \quad (11)$$

$$\frac{D_{12}}{a^2} = \frac{D_1'}{a^2} \frac{q_2}{q_1} \frac{\delta \ln p_1}{\delta \ln q_2} \quad (12)$$

$$\frac{D_{21}}{a^2} = \frac{D_2'}{a^2} \frac{q_2}{q_1} \frac{\delta \ln p_2}{\delta \ln q_1} \quad (13)$$

$$\frac{D_{22}}{a^2} = \frac{D_2'}{a^2} \frac{\delta \ln p_2}{\delta \ln q_2} \quad (14)$$

For instance, $Ksav$ is related to D in single adsorbate case as

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

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