

SORPTION ON A MICROPOROUS CARBON MEASURED WITH THE NOVEL TECHNIQUE TEOM

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Introduction

A new apparatus has been used to measure adsorption and diffusion in microporous materials, namely the tapered element oscillating microbalance (TEOM). The essential feature of the TEOM technique is an oscillating element that is based on inertial forces instead of weight to measure the mass adsorbed. One of the major advantages of this technique is that the experimental data are not influenced by factors such as buoyancy and flow patterns. The TEOM is described elsewhere in more detail by Zhu et al. [1]. Uptake experiments were performed with n-butane on Kureha carbon. The adsorption and desorption profiles were very asymmetrical. The results are reported here of developing a model that describes both adsorption and desorption with one set of parameters.

Experimental

The carbon used is a microporous activated carbon obtained from Kureha, Japan. This carbon consists of perfect spheres and can be classified as a carbon molecular sieve. It has a very narrow micropore size distribution around 0.5 nm and contains hardly any macropores. The sorption experiments were performed with a sample mass of 10.8 mg Kureha, at a temperature of 303 K, and a total system pressure of 1.0 bar. The butane feed was introduced and stopped again as a step input during adsorption and desorption, respectively. The concentration of n-butane was 86.8 g/m³ at a total flow rate of about 100 ml/min, resulting in an n-butane supply rate of 8.5 mg/min.

Results and discussion

The adsorption and desorption profiles are given in Figure 1. It is seen that a large difference exists between the time scale of adsorption and desorption. During adsorption equilibrium was reached already after about 40 s, whereas the desorption took more than 1000 s. The diffusion process is described with the Maxwell-Stefan theory for surface diffusion [2]. Taking only surface or micropore diffusion into account, the continuity relation for spherical particles becomes

$$\frac{\partial \theta}{\partial t} = D^s \frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \Gamma \frac{\partial \theta}{\partial r} \right) \quad (1)$$

$$D_F = D^s \Gamma \quad (2)$$

where θ is the adsorbate occupancy, D^s is the Maxwell-Stefan surface diffusivity, Γ is the thermodynamic factor, and D_F is the Fick surface diffusivity. The thermodynamic factor depends on the type of isotherm used, through the derivative of the gas phase pressure to the fractional surface occupancy. So, it is obvious that various isotherm models give a different adsorbed concentration dependency for the Fick surface diffusivity [3]. The Langmuir and the Dubinin-Radushkevich isotherm equations were used in the modeling of the sorption curves. The diffusivities that were obtained with the two adsorption isotherm models were not the same. Furthermore, adsorption and desorption could not be described with the same diffusivity whether Langmuir or Dubinin-Radushkevich was applied.

As one likes to describe adsorption and desorption with the same set of diffusivity parameters, the model was further adjusted. Because desorption was so much slower than adsorption, an activated diffusivity as function of the occupancy was introduced. The Maxwell-Stefan surface diffusivity was correlated with the isosteric heat of adsorption, $q^{st}(\theta)$,

$$D^s = D_0 \exp\left(\frac{-q^{st}(\theta)}{aRT}\right) \quad (3)$$

where a is a fit parameter to regulate the exact dependence of the diffusivity on the isosteric heat of adsorption. The isosteric heat of adsorption is a function of the occupancy, and was calculated with the Dubinin-Radushkevich adsorption isotherm model. The isosteric heat increases with decreasing occupancy implying that at low occupancies more energy is needed for desorption. The simulation results are shown in Figure 1. It is seen that adsorption and desorption can be described well with the same set of parameters.

Conclusions

Sorption experiments were performed with the TEOM apparatus. The adsorption and desorption profiles for n-butane on Kureha were very asymmetrical. Correlating the diffusivity with the isosteric heat of adsorption enabled the description of both adsorption and desorption with the same set of diffusivity parameters.

References

- [1] Zhu W, Van de Graaf JM, Van den Broeke LJP, Kapteijn F, Moulijn JA. TEOM: a unique technique for measuring adsorption properties. Light alkanes in silicalite-1. *Ind Eng Chem Res* 1998;37: 1934-1942.
- [2] Krishna R. A unified approach to the modelling of intraparticle diffusion in adsorption processes. *Gas Sep Purif* 1993;7:91-104.
- [3] Linders MJG, Van den Broeke LJP, Van Bokhoven JJGM, Duisterwinkel AE, Kapteijn F, Moulijn JA. Effect of the adsorption isotherm on one- and two-component diffusion in activated carbon. *Carbon* 1997;35:1415-1425.

Notation

- θ Adsorbate occupancy, -
- t Time, s
- r Radial position in sorbent particle, m
- D^s Maxwell-Stefan surface diffusivity, m^2/s
- Γ Thermodynamic factor, -
- D_F Fick surface diffusivity, m^2/s
- D_0 Pre-exponential factor, m^2/s
- q^{st} Isosteric heat of adsorption, J/mol
- R Gas constant, J/(mol.K)
- T Temperature, K
- a Fit parameter, -

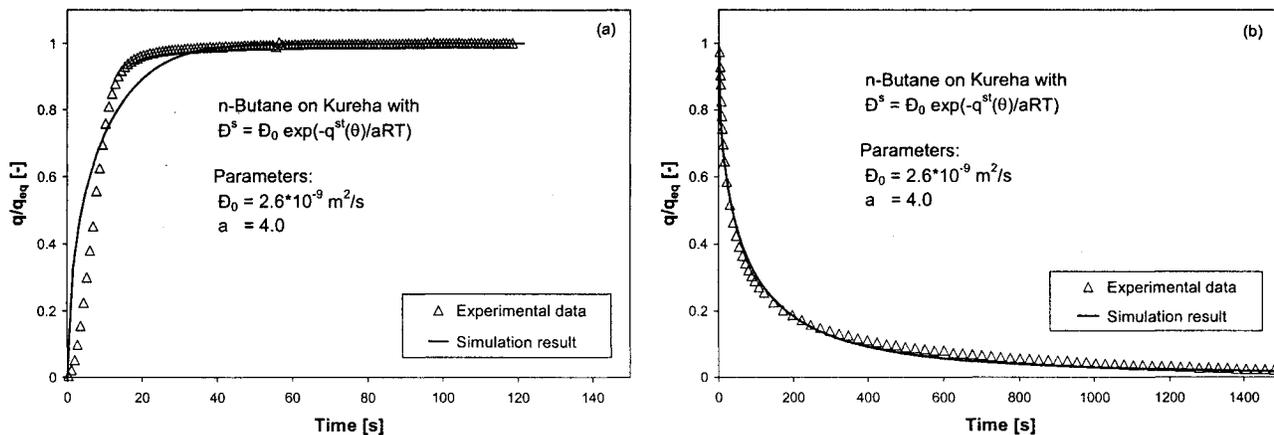


Figure 1: Sorption of n-butane on Kureha at 303 K. (a) Adsorption, (b) desorption. The Maxwell-Stefan theory for surface diffusion is used to model the experimental data. The diffusivity is correlated with the isosteric heat of adsorption. The curves are scaled with the equilibrium occupancy.