

KINETICS OF *n*-OCTANE VAPOR ADSORPTION AND DESORPTION ON AN ACTIVATED CARBON

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Introduction

Activated carbons are often used for the adsorption of environmentally unfriendly organic species from both gas and liquid phases. Activated carbons have both hydrophilic and hydrophobic sites, the latter being used for hydrocarbon adsorption. Isotherms are a function of the distribution of the adsorption sites, porosity and pressure. Kinetics are critically important in assessing carbon bed performance [1-3], and here we report the adsorption characteristics of *n*-octane on an activated carbon with special emphasis on the kinetics.

Experimental

Adsorption of *n*-octane on BAX950, wood-based active carbon, was studied using an 'Intelligent Gravimetric Analyzer' (IGA) from Hiden Analytical Ltd. 100 ± 1 mg, of carbon was outgassed until it reached constant weight (at $\sim 10^{-6}$ Pa). Adsorption/desorption isotherms were obtained at temperatures in the range 288–313 K for pressure steps in the range $p/p^\circ = 0-0.97$. Subsequent adsorption kinetics were determined using vapor uptake for each relative pressure step.

Kinetic Models

The linear driving force (LDF) mass transfer and the combined barrier resistance/diffusion models were used to analyze the adsorption kinetics of *n*-octane on BAX950. The LDF model is described by the following equation:

$$\frac{M_t}{M_e} = 1 - e^{-kt}$$

where M_t is the uptake at time t , M_e is the equilibrium uptake both in arbitrary mass units, t is the time (s) and k is the rate constant (s^{-1}). Hence a plot of $\ln(1 - M_t/M_e)$ versus time will be linear with a gradient equal to the rate constant.

The combined barrier resistance/diffusion model is based on the existence of a surface barrier with subsequent diffusion being governed by Fick's law:

$$D \frac{\partial C}{\partial r}(r_c, t) = k_b \{C^*(t) - C(r, t)\}$$

where k_b is the barrier resistance (cm s^{-1}), C the sorbate concentration (mmol cm^{-3}), r_c the crystallite radius (cm), t is time (s), D the diffusivity ($\text{cm}^2 \text{s}^{-1}$), r the radial co-ordinate and C^* the surface concentration in equilibrium with the gas phase. The model yields the barrier resistance constant, k_b and k_d , which equals D/r_c^2 . Both models are fitted to experimental data by finite element methods.

Results and Discussion

Dubinin–Radushkevich analysis of the isotherm (Figure 1) shows a deviation from linearity indicating adsorptive filling beyond micropore distribution function used in the D–R model. Extrapolation to $p/p^\circ = 1$ gives a pore volume of $0.85 \text{ cm}^3 \text{ g}^{-1}$. Isothermic heats of adsorption decreased approximately linearly as surface coverage increased with values between 43–62 kJ mol^{-1} . The limiting isothermic heat at zero surface coverage of 68 kJ mol^{-1} compares to 38.6 kJ mol^{-1} for heat of vaporization. All adsorption and desorption kinetics for $p/p^\circ < 0.175$, follow a linear driving force mass transfer (LDF) model (Figure 2). At $p/p^\circ > 0.175$ a barrier-resistance/diffusion model was obeyed (Figure 3).

Activation energies calculated for $p/p^\circ = 0-0.175$ show highest values occur at low p/p° , with a maximum at $p/p^\circ \sim 0.075$ (Figure 4). The activation energies cover a range $\sim 15-40 \text{ kJ mol}^{-1}$. An initial large value is due to filling of ultramicroporosity, a decrease is observed with filling of micropores (upto $p/p^\circ = 0.005$, a micropore volume of $\sim 0.22 \text{ cm}^3 \text{ g}^{-1}$). The activation energy maximum occurs at the same p/p° for the deviation observed in the D–R plot. The pore size distribution contains supermicroporosity and mesoporosity, and it is reasonable to conclude that the activation energy maximum is related to this fact. The peak results from an increased diffusional barrier as pore-filling co-operative effects cause restricted access to pores. Adsorption rate increases with p/p° and surface coverage. As the microporosity fills, the rate increases. The isothermic heats decrease, indicating surface diffusion into pores increases with increasing surface coverage. Desorption rate constants decrease with lower p/p° , suggesting desorption becomes less favorable. As

pressure decreases, the desorption rate becomes very small suggesting difficulty in desorbing the long chain alkane from micropores.

Conclusions

Both adsorption and desorption kinetics follow a LDF rate law for > 90% of the sorption process, for $p/p^{\circ} = 0-0.175$. The rate of adsorption varies with position on the isotherm and hence the mechanism of the adsorption process. Activation energies for adsorption are highest initially, at low p/p° where molecular sieving into microporosity occurs. Activation energy for adsorption reaches a maximum at $p/p^{\circ} \sim 0.075$, with the barrier ascribed to increased diffusional resistance in the carbon due to pore-filling co-operative effects. The dynamics of *n*-octane vapor adsorption provide an insight into the kinetic requirements of an activated carbon filter for the removal of VOCs from the atmosphere at very low concentrations.

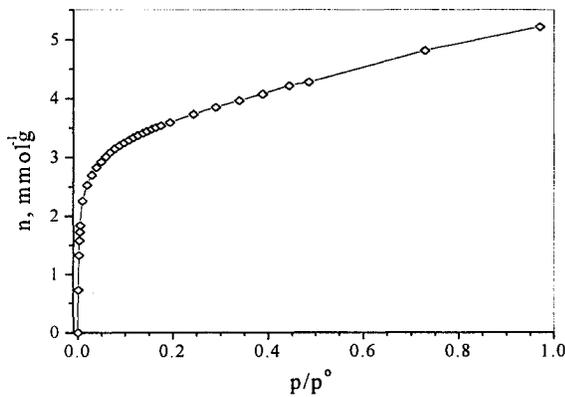


Figure 1. Adsorption isotherm for *n*-octane on BAX950, at 293 K.

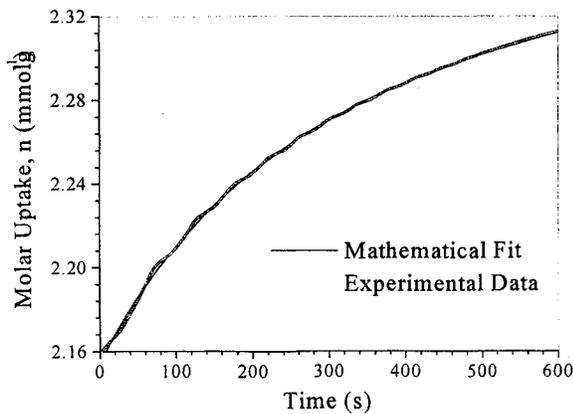


Figure 2. LDF fit for *n*-octane adsorption on BAX950 at 298 K, $p/p_o = 0.00486-0.00973$.

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 - [3] Reid CR, Thomas KM. Adsorption of gases on CMS used for air separation: linear adsorptives as probes for kinetic study. *Langmuir* 1999;MS #LA981289.

Acknowledgments

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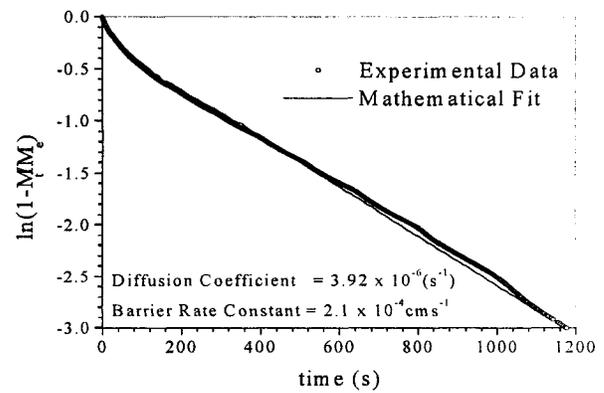


Figure 3. Combined barrier-resistance/diffusion model fit for adsorption of *n*-octane on BAX950 at 298 K, $p/p_o = 0.48643-0.72964$.

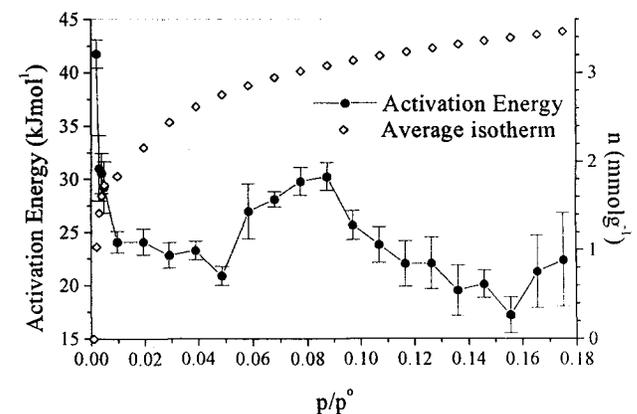


Figure 4. Activation energies for *n*-octane adsorption on BAX950 (288–313 K).