Adsorption of Ethylene in Beds of Activated Carbon

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As indicated in earlier studies (Andrieu and Smith, 1980, 1981) there is a lack of information on rate and equilibrium parameters for adsorption of gases on activated carbon. In the prior work data were obtained from carbon dioxide, hydrogen sulfide and sulfur dioxide on type BPL (Pittsburgh Activated Carbon Co.) activated carbon. This material is made by binding micro particles of bituminous coal prior to activation. Reported here are parameters for adsorption of ethylene on the same activated carbon. These results for a hydrocarbon and the earlier values for inorganic gases provide useful information for design of adsorption columns for separating gases.

The usual model for describing adsorption in a packed bed of adsorbent particles includes axial dispersion, gas-to-particle mass transport, intraparticle diffusion and adsorption at an interior site. However, some activated carbons have a very broad pore-size range. Analysis of intraparticle diffusion for such carbons has been interpreted most satisfactorily (Chihara et al., 1978) by dividing diffusion into macropore and micropore processes. Transport in the macropores (diameter $> 50 \times 10^{-10}$ m, average diameter $= 75 \times 10^{-8}$ m) for BPL carbon is assumed to be by Knudsen and bulk diffusion. In the much smaller micropores ($< 50 \times 10^{-10}$ m, average diameter $= 22 \times 10^{-10}$ m) where molecule-wall interaction predominates, diffusion is supposed to occur by an activated, surface process.

For application to column design the most important parameters are the adsorption equilibrium constant K_A and the intraparticle diffusivities D_a and D_i. Axial dispersion and gas-to-particle mass transport effects are usually small in commercial columns, and the intrinsic rate of adsorption of ethylene at an interior site is relatively rapid so that equilibrium may be assumed.

As in the earlier studies, pulse-response curve measurements were analyzed by the method of moments to obtain K_A, D_a and D_i. In our case pulses of 3% ethylene in helium were introduced into a helium stream entering the bed of carbon particles. The precautions necessary to obtain suitable data, method of analysis, as well as details about the apparatus, were presented by Andrieu and Smith (1980). Hence, only the results are given here. The pore-volume distribution curve for BPL carbon (Andrieu and Smith, 1981), operating conditions, column void fractions and packing methods, and other details of the experimental procedure are available (Cavalletto, 1981). Response curves were measured over a range of gas velocities and for three particle sizes.

ADSORPTION EQUILIBRIUM RESULTS

Equilibrium constants are calculated from corrected first moments, $\Delta\mu_1$, of the response peaks. The corrected moment is obtained by subtracting μ_1 for a nonadsorbable tracer (helium) from the first moment for ethylene, thus eliminating dead volume effects. Measured first moments $(\mu_1)_{exp}$ for both ethylene and for helium are shown in Figure 1. The first-moment function corrected for void fraction variations from column to column, as plotted in Figure 1, should be independent of carbon particle size. Hence, the agreement between the data points for different particle sizes is a measure of the reproducibility and accuracy of the experimental results. From the K_A values at the three temperatures, isoteric heats of adsorption can be calulated from the van't Hoff equation. The results for ethylene as well as those obtained earlier for CO_2, H_2S and SO_2 are summarized in Table 1. The temperature range 443-483 K for the ethylene results was chosen so as to give rapidly reversible adsorption; the response curves did not have long tails which introduce errors in the moments. The K_A values are a measure of adsorption capacity. A comparison at a common temperature of 343 K, gives

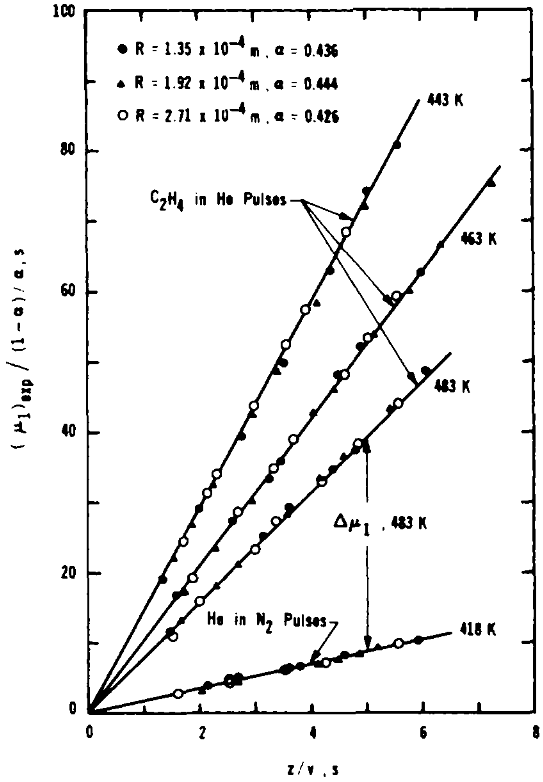

Figure 1. First moment results.

	K_A, m³/kg
SO_2	2.0
H_2S	0.19
C_2H_4	0.185 (extrapolated)
CO_2	0.040

The adsorption capacity of this activated carbon for ethylene is seen to be about the same as that for H_2S, but less than that for SO_2 and greater than the capacity for CO_2. Also, from Table 1 the heat of adsorption for ethylene is about the same as that for H_2S and less than $-\Delta H_A$ for SO_2. The ratio of the heat of adsorption to the heat of condensation (at the normal boiling point) is about 2.4 for ethylene, while this ratio is from 1.0 to 1.6 for CO_2, H_2S and SO_3. This comparison indicates a stronger carbon site interaction, relative to intermolecular interaction, for ethylene than for the oxygen-containing gases.

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TABLE 1. ADSORPTION EQUILIBRIUM RESULTS

Ethylene				
Temp., K	443	463	483	
K_A, m^3/kg	0.015	0.010	0.0073	
Carbon Dioxide				
Temp., K	303	313	338	358
K_A, m^3/kg	0.13	0.090	0.048	0.028
Hydrogen Sulfide				
Temp., K	323	343	363	
K_A, m^3/kg	0.37	0.19	0.11	
Sulfur Dioxide				
Temp., K	373	393	408	423
K_A, m^3/kg	0.67	0.34	0.22	0.15

	Heat of Adsorption $-\Delta H_A$, kcal/mol
Ethylene	7.6
Carbon Dioxide	6.0
Hydrogen Sulfide	7.1
Sulfur Dioxide	9.5

INTRAPARTICLE DIFFUSIVITIES

After eliminating the influence of axial dispersion and gas-to-particle mass transfer, intraparticle diffusivities can be evaluated from the second moments of the response curves. The precision of these moments did not permit determination of an accurate effect of temperature on diffusivity. Values for macropore diffusivity, D_a, and the corresponding tortuosity factor, τ_a, in the range 463-483 K varied from 1.2 to 2.7 × 10^{-6} m^2/s and 6.6 to 15, respectively. Diffusion in the macropore region was considered to include pore diameters greater than 50×10^{-10} m, for which the average diameter is 75×10^{-8} m. Diffusion in these large pores is predominantly in the pore volume. Hence, it may be appropriate to interpret D_a values in terms of a tortuosity factor calculated from the equation

$$\tau_a = \frac{\epsilon_a D}{D_a} \tag{1}$$

Here D is a composite diffusivity accounting for both bulk and Knudsen diffusion. Such values of τ_a should be independent of the diffusing substance and of temperature. They also are a very sensitive measure of the accuracy of the second moments. Tortuosity factors determined from CO_2 data were about 4.5, from H_2S about 5, and from SO_2 about 6.5 (Andrieu and Smith, 1980, 1981). The average for our results for ethylene is higher. All of the results indicate that the tortuosity factor is larger (corresponding to lower effective diffusivity) for our activated carbon than for a particle with a narrow pore size distribution. Thus, for silica gel, or macroporers in alumina pellets, τ_a is of the order of 4 (Satterfield, 1970). We believe that the lower than expected diffusivities in the carbon is due to the very broad size range with multiple peaks. The pore-volume distribution curve (Andrieu and Smith, 1981) has three peaks. This suggests that the use of an average for radius for evaluating the Knudsen diffusivity in the macro-pore region is inaccurate. The deviation in τ_a values between gases may mean that molecular shape and the force field around the adsorbate molecules may affect diffusion, even in the macropore region.

In application, these results mean that intraparticle diffusion has a significant effect on the global rate of adsorption and should be accounted for in the design of separation processes. It also means that reducing particle size improves adsorption rates, and that pore-size distribution data are necessary for careful design using some activated carbons.

The radius of the microparticles used to prepare the activated carbon is unknown. However, as a basis for comparison, a micropore diffusivity, D_i, can be estimated from the second-moment values by assuming a radius equal to 10×10^{-6} m. The resulting, approximate D_i is about 1×10^{-9} m^2/s. For an average micropore radius of 11×10^{-10} m, the Knudsen diffusivity would be 4×10^{-7} m^2/s. Since D_i is much smaller than this Knudsen diffusivity, it is concluded that diffusion in the very small micropores occurs by a hindered molecule-wall interaction. This is in agreement with the interpretation of Chihara et al. (1978) for transport in small pores of activated carbon and also was found applicable for adsorption of CO_2, H_2S and SO_2.

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NOTATION

D = composite diffusivity = $(1/D_{EH} + 1/D_{KE})^{-1}$, m^2/s
D_a = effective diffusivity in macropores (> 50×10^{-10} m diameter), m^2/s
D_{EH} = bulk diffusivity in ethylene-helium system, m^2/s
D_i = effective diffusivity in micropores (< 50×10^{-10} m diameter), m^2/s
D_{KE} = Knudsen diffusivity for ethylene, m^2/s
ΔH_A = isoteric heat of adsorption, kcal/mol
K_A = adsorption equilibrium constant, m^3/kg
R = particle radius, m
T = absolute temperature, K

Greek Letters

α = void fraction of the bed of carbon particles
ϵ_a = macropore porosity of the activated carbon ($\epsilon_a = 0.3$ for pores > 50×10^{-10} m diameter)
τ_a = tortuosity factor for the macropores
$(\mu_1)_{exp}$ = first moment (average retention time) of the pulse, determined from the measured response curve, s
$\Delta\mu_1$ = $|(\mu_1)_{C_2H_4} - (\mu_1)_{He}|_{exp}$, s

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