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AN EXPERIMENTAL STUDY OF ADSORPTION INTERFERENCE IN
BINARY MIXTURES FLOWING THROUGH ACTIVATED CARBON

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ABSTRACT

We measured the isothermal transmission through activated carbon adsorber beds at 25°C of two binary mixtures (viz., acetaldehyde-propane and acetylene-ethane) in a helium carrier gas. The transmission of each component in the mixture is the ratio of the outlet concentration to the inlet concentration. The inlet concentration of each component was in the range between 10 and 500 ppm. The constant inlet volumetric flow rate was controlled at 200 cc (STP)/min in the acetaldehyde-propane experiments and at 50 cc(STP)/min in the acetaldehyde-ethane experiments. Comparison of the experimental results with the corresponding single-component experiments under similar conditions revealed interference phenomena between the components of the mixtures as evidenced by changes in both the adsorption capacity and the dispersion number; more specifically, throughout the range of concentrations studied here, we observed that propane displaces acetaldehyde from the adsorbed state. This displacement is manifested by the fact that the acetaldehyde transmission exceeds unity at some stage. We observed also that the outlet concentration profiles of propane in the binary mixtures tend to become more diffuse than the corresponding concentration profiles of the one-component experiments. We observed similar features with the binary mixtures of acetylene and ethane; in this case, the displacement of acetylene by ethane is less pronounced because of the low adsorptivity of both compounds.

THEORETICAL BACKGROUND

The adsorption of gases and vapors on porous solids is a process with numerous applications (e.g., in separation techniques). Separations are achieved by allowing a gas stream to flow through an adsorber bed. The performance study of an adsorber bed usually involves the so-called "breakthrough" or "transmission" curve, i.e., the normalized outlet concentration of a particular species versus the time (or the eluted volume). The shape of the transmission curve is strongly determined by (a) the equilibrium relation between the (stationary) solid-phase concentration and the (moving) fluid-phase concentration, and by (b) the overall rate of adsorption.^{1,2,3} In this paper, we confine our discussion to the

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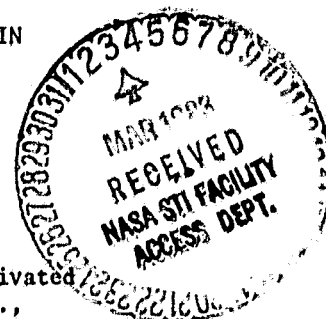
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isothermal transmission of a step-input concentration flowing steadily through an initially clean adsorber bed. The problem then consists of integrating the mass-balance equation along with the rate equations. Since mathematical difficulties posed by the rate equations preclude a general solution, simplifying assumptions become necessary. The analysis is simplified by assuming a linear equilibrium relation between the solid-phase and liquid-phase concentrations (i.e., a linear isotherm). Several authors have presented analytical solutions based on different diffusion mechanisms for the transmission of a single species; for example, Thomas⁴ assumed that the adsorption rate is controlled by the diffusion from the bulk of the fluid to the external surface of the solid (external mass transfer). Lapidus and Amundson⁵ obtained solutions for external mass transfer and axial diffusion. Rosen⁶ considered both external mass transfer and diffusion in the solid phase, while Masamune and Smith⁷ combined external, surface, and intraparticle diffusion.

For concave isotherms, the transmission curves become broader with increasing bed length; while for convex isotherms, the transmission curves tend to attain a constant pattern as the bed length increases. This constant pattern behavior was utilized by several authors⁸⁻¹² to simplify the mathematical problem while others utilized powerful numerical techniques.¹³⁻¹⁵

The situation is more complex for multicomponent adsorption because it is necessary to deal with a system of coupled equations describing each component of the mixture. Assuming non-dispersive adsorption, Glueckauf¹⁶ presented analytical results for two-component mixtures. Cooney and Lightfoot¹⁷ and Cooney and Struss¹⁸ extended Glueckauf's work by including a mass-transfer term together with the constant-pattern approximation. Weber and Crittenden¹⁹ and Hsieh et al²⁰ developed numerical methods for more general conditions.

EXPERIMENTAL TECHNIQUE

We measured the isothermal transmission through activated carbon adsorber beds of two binary gas mixtures, namely acetaldehyde-propane and acetylene-ethane in a helium carrier gas. The transmission of each component of the mixture is the ratio of the outlet concentration to the inlet concentration. The cylindrical adsorber beds were packed with "Columbia" type 4LXC 12/28 activated carbon. The adsorber bed temperature was 25°C and was controlled to ± 20 millidegrees by means of a dual-bath constant-temperature system. The experimental apparatus is shown in Fig. 1. The flow system is constructed of stainless-steel tubing and valves with teflon seats and gaskets. Flow controllers FCA, FCB and FCC enable setting of the gas flow rate from cylinders A, B and He (usually Helium), while rotameters RA, RB, RC and RD give an approximate value of the flow rate. Three-way ball valves B1, B2, B3, and B4 can divert the flow to the electronic dual-

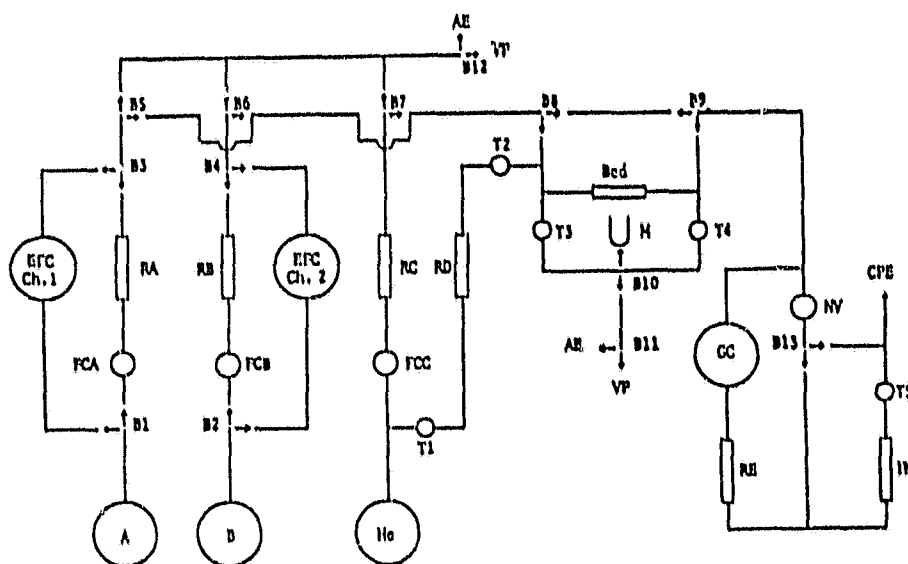


Fig. 1. Schematic diagram of the flow system

channel mass-flow controller, which controls the flow rate to ± 1 percent. The flow meter FM measures the flow rate with an accuracy of ± 0.5 percent. Three-way ball valves B5, B6 and B7 enable mixing of the three gas streams; while similar valves B8 and B9 permit two modes, namely flow through the adsorber bed, and flow bypassing the adsorber bed. The manometer M along with the toggle valves T3 and T4 are used to measure the pressure drop across the bed. Typical values for the pressure drop ranged between 10 and 20 mm Hg, while the total pressure in the adsorber bed ranged between 740 and 780 mm Hg. The automatic data-acquisition system, which is located downstream from the adsorber bed, consists of an automated sampling valve, a gas chromatograph with a flame ionization detector, and a digital integrator. With this apparatus we measured the time-dependent concentration $C(t)$ at the outlet of the adsorber bed. The concentration of each gas was known within ± 1 percent. The concentration of each gas was checked against a primary standard mixture before and after each series of experiments; no appreciable drift was observed. In the acetaldehyde-propane experiments, we used an adsorber bed (10 cm long and 0.454 cm i.d.) packed with 0.569 g of carbon; whereas in the acetylene-ethane experiments, we used an adsorber bed (40 cm long and 0.486 cm i.d.) packed with 2.638 g of carbon. At the end of each experiment, the saturated adsorber bed was desorbed by allowing high-purity helium to flow through the bed at a rate of

100 to 200 cc/min for 14 hours, and simultaneously heating the adsorber to 150°C. Sufficient time was allowed before the beginning of each experiment to ensure thermal equilibrium. In these experiments, we used low-concentration mixtures to minimize non-equilibrium effects caused by the heat of adsorption.

The transmission curves for three binary gas mixtures of acetaldehyde and propane in a helium carrier gas are shown in Fig. 2. The concentrations of acetaldehyde and propane in parts per million (ppm) were (a) 90 and 12, (b) 66 and 34, and (c) 33 and 67, respectively. The volumetric flow rate was 200 cc (STP)/min for all three experiments. We note that the transmission of acetaldehyde exceeds unity over a certain range of eluted volume; or equivalently, the outlet concentration of acetaldehyde exceeds the inlet concentration. This phenomenon (sometimes called "rollover") occurs because propane displaces acetaldehyde from the adsorbed phase to the gas phase. At a sufficiently large eluted volume, the adsorber becomes saturated and the transmission of both components reaches unity. It should be noted also that the overall slope of the propane transmission curves decreases with decreasing propane concentration; or equivalently, the overall dispersion for propane increases with increasing acetaldehyde concentration. This phenomenon should be attributed to the displacement of acetaldehyde by propane; however, the acetaldehyde transmission curve does not show any substantial change in slope.

The adsorption capacity K in cc(STP)/g for each component can be evaluated from the transmission curve by means of the general formula

$$K = \frac{C_0}{m} \int_0^{\infty} [1 - T(V)] dV \quad (1)$$

where C_0 is the inlet concentration, m the mass of the adsorber in grams, $T(V)$ is the transmission and V is the eluted volume in cc(STP). This integration was carried out numerically, and the results are summarized in Table I. Also listed in Table I are

Table I. Adsorption capacities in cc(STP)/g of activated carbon at 25°C for single-component gases (K_1) and binary mixtures (K_2).

Binary Mixture	C (ppm)	K_1	K_2
Acetaldehyde	90	3.13	2.87
Propane	12	0.65	0.54
Acetaldehyde	66	2.50	2.30
Propane	34	1.60	1.43
Acetaldehyde	33	1.43	1.21
Propane	67	2.64	2.61

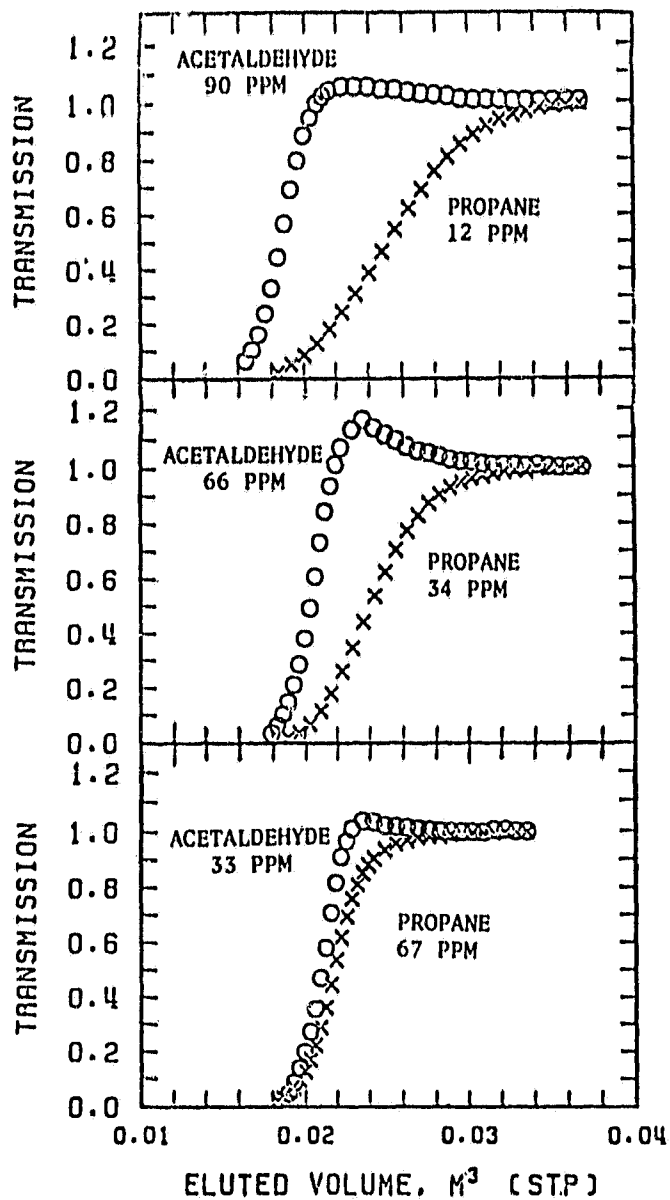


Fig. 2. Transmission of binary mixtures of acetaldehyde and propane in helium through an adsorber bed at 25°C packed with activated carbon.

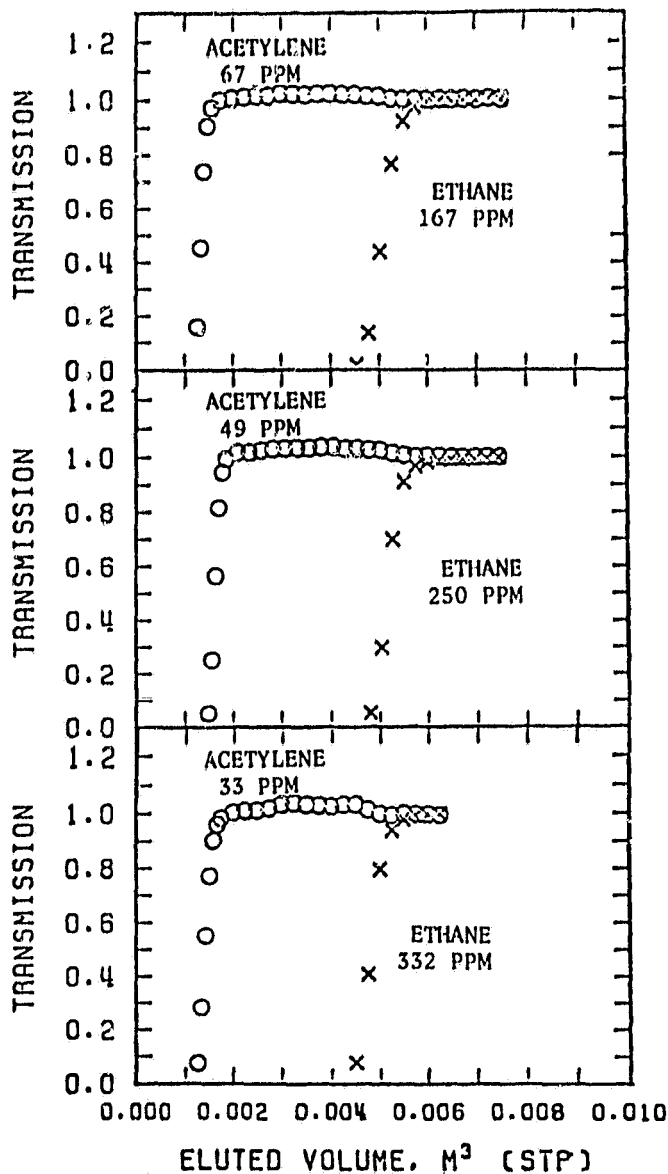


Fig. 3. Transmission of binary mixtures of acetylene and ethane in helium through an adsorber bed at 25°C packed with activated carbon.

the adsorption capacity values obtained from single-component adsorption experiments. Comparison of the corresponding values in the single-component experiments and binary-mixture experiments reveals a substantial reduction of the adsorption capacity for both components in the binary mixture. This reduction is a result of competitive adsorption. The situation is different in the acetylene-ethane binary mixtures. The transmission curves for three mixtures are shown in Fig. 3. The concentrations of acetylene and ethane in ppm are (a) 67 and 167, (b) 49 and 250, and (c) 33 and 332, respectively. The volumetric flow rate was 50 cc(STP)/min for all three experiments. Here acetylene breaks through first, and is displaced by ethane, as indicated by the "rollover"; however, the locations and slopes of the transmission curves do not vary appreciably for the three mixtures. This result should be attributed to the low adsorptivities of both components of the mixture. It should be mentioned also that the overall slope of the ethane transmission curve is equal to that of the single-component transmission curve under the same experimental conditions. This result is compatible with the findings of Shen and Smith,²¹ who examined the rates of adsorption in a benzene-hexane binary mixture. They found that in the linear isotherm range the rate of adsorption of benzene from mixtures was the same as in single-component adsorption. It should be pointed out that in the range of concentrations examined here, acetylene obeys a linear isotherm,²² while the adsorption of ethane does not deviate appreciably from the linear shape.²³

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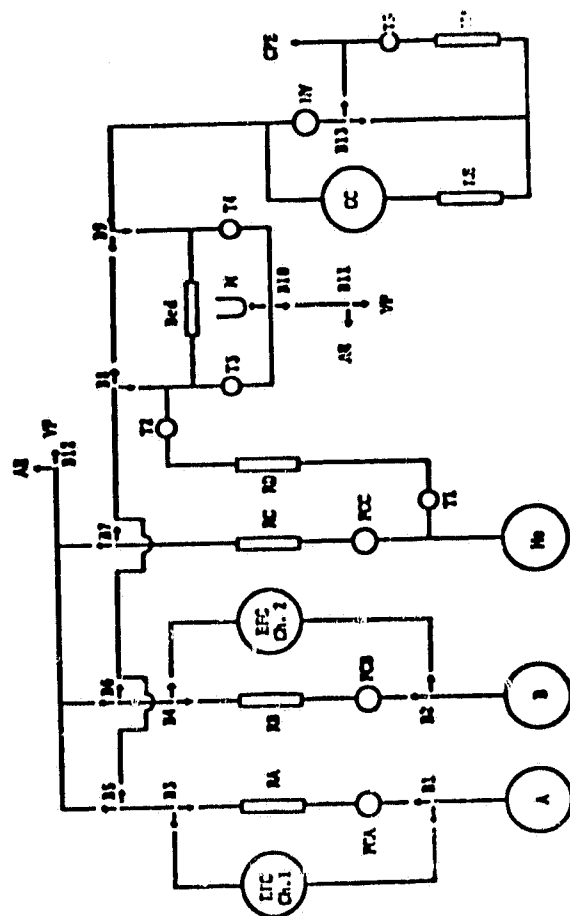


Fig. 1

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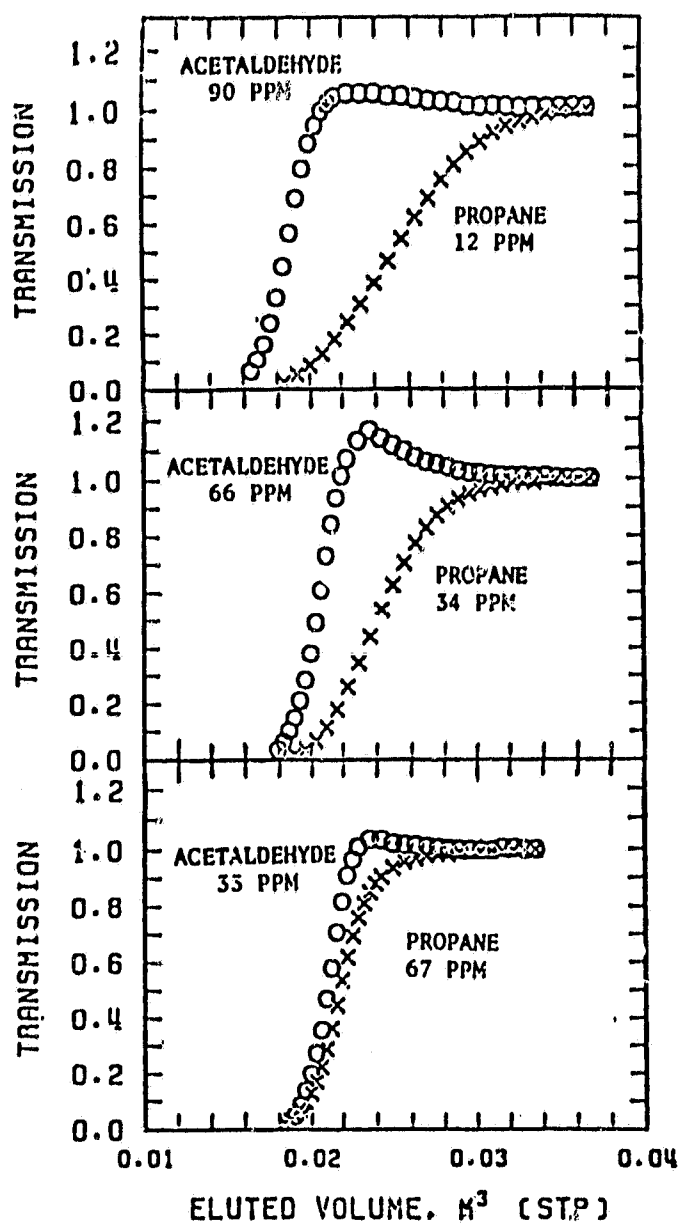


Fig. 2

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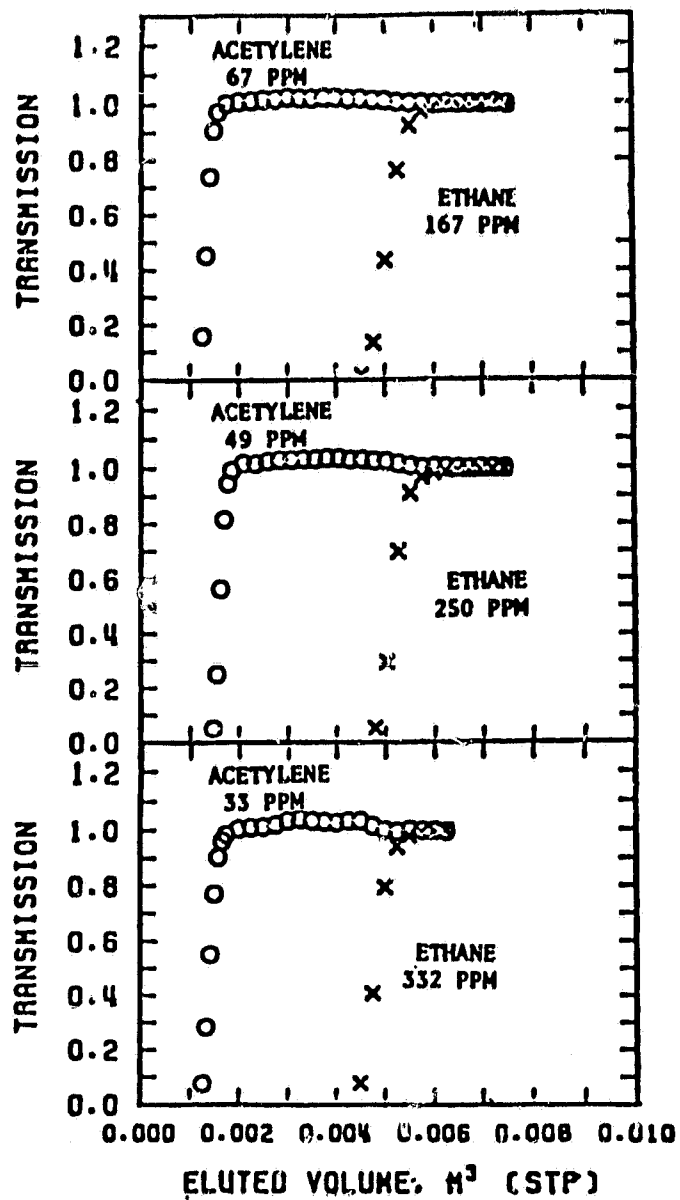


Fig. 3