Chromatographic Study of Alkanes in Silicalite: Equilibrium Properties

Jeffrey R. Hufton and Ronald P. Danner
Dept. of Chemical Engineering, The Pennsylvania State University, University Park, PA 16802

Variations of perturbation chromatography were used to measure Henry's constants and equilibrium isotherms of various gases on silicalite. Three different adsorbent samples were analyzed (commercial powder and extruded pellets, and laboratory-synthesized crystals), and no discernable differences among the measured parameters were noted. Henry's constants for the linear alkanes were determined from isobaric and nonisobaric chromatography experiments. They were correlated successfully with temperature and the number of carbon atoms per adsorbate molecule. Isotherms were measured from concentration pulse or tracer/concentration pulse chromatography techniques. The Flory-Huggins version of the vacancy solution model was used to correlate pure gas isotherms and predict binary behavior successfully.

Introduction

The use of adsorption-based processes for purifying or separating gas mixtures has been facilitated by the development of new solid adsorbents and more efficient adsorption cycles (for example, pressure swing adsorption). Operation of most of these units depends on at least one of the components of the gas mixture being adsorbed more strongly than the others at equilibrium. Accurate equilibrium data are crucial for the proper design of these systems. This type of data is not easy to obtain via traditional experimental techniques since both gas- and adsorbed-phase compositions must be determined. For this reason, a number of adsorption equilibrium models have been developed to predict multicomponent behavior from pure component data (Myers and Prausnitz, 1965; Ruthven et al., 1973; Cochran et al., 1985). This article deals with the measurement of pure and binary adsorption isotherms using different versions of the chromatographic technique. Comparisons with an equilibrium adsorption model were then made to test the utility of the theoretical model for alkane/silicalite systems.

Another goal of this work was to measure and correlate equilibrium behavior of infinitely-dilute adsorbates in different samples of adsorbent. This is commonly characterized by Henry's constant, which is equal to the slope of the adsorption isotherm at low adsorbate pressure. These parameters are important when designing industrial processes for the removal of low levels of impurities from a gas stream. A correlative equation based on these data would be particularly useful since it might facilitate rapid extrapolation to other adsorbates. Henry's constants also reflect the strength of adsorbate-adsorbent interactions, since at these conditions adsorbate-adsorbate effects are eliminated. Thus, changes in adsorbent properties resulting from different sample origins should be evident in the analysis of Henry's constant data.

A number of investigators have measured the equilibrium behavior of aromatics in silicalite (Wu et al., 1983; Pope, 1986; Shah et al., 1988; Zikanova et al., 1987). Others have been interested more in studying the transport properties of adsorbate in the channel network of silicalite (for example, Eic and Ruthven, 1989; Hayhurst and Paravar, 1988; van den Begin et al., 1989; Caro et al., 1985). The present work deals primarily with the adsorption equilibria of alkanes in silicalite. Stach et al. (1983) and Thamm (1987) measured differential heats of adsorption of these compounds, among others, in silicalite via calorimetry. Smaller alkanes exhibited a fairly constant heat of adsorption with increasing adsorbed-phase loading, thus indicating a relatively homogeneous adsorbent. Stach et al. (1986) later presented adsorption isotherms of hydrocarbons on silicalite derived from static uptake experiments. Lechert and Schweitzer (1983) measured equilibrium isotherms and differential heats of adsorption for butane on laboratory-syn-

---

Correspondence concerning this article should be addressed to R. P. Danner.

J. R. Hufton is presently at the Department of Chemical Engineering, University of New Brunswick, Fredericton, NB, Canada E3B 5A3.

thesized silicalite. The solid crystals were coated on glass spheres, which were subsequently packed into a column and analyzed chromatographically. Chiang et al. (1984b) also used the concentration pulse chromatography technique to measure Henry's constants of light alkanes on commercial silicalite powder. Hufton and Danner (1991) reported an adsorption isotherm for ethane on a pelletized form of this same material. The chromatographic technique was also employed in this study; however, the system was investigated with an isotopically labeled ethane pulse (tracer pulse chromatography).

The above studies were carried out for pure gas systems only—multicomponent gas mixtures on silicalite have not been studied as extensively. Wang et al. (1986) measured binary isotherms of carbon dioxide and ethylene on an adsorbent structurally similar to silicalite (ZSM-5). More recently, Abdul-Rehman et al. (1990) measured pure, binary, ternary and quaternary isotherms for C_1-C_4 alkane mixtures at 300 K and 345-655 kPa. They found that the experimental data were satisfactorily described by the Toth isotherm.

Experimental Method

The two types of chromatography implemented in this study, concentration pulse and tracer pulse, were discussed previously by Hufton and Danner (1991). For clarity, these techniques are described briefly below.

Concentration pulse chromatography (CPC) is analogous to the familiar analytical technique frequently used to determine chemical compositions. In its simplest form, a pulse of adsorbate is injected into an inert carrier gas (such as helium), which passes through a column packed with regenerated adsorbent. A suitable detector, often either a thermal conductivity or flame ionization detector, measures the concentration of adsorbate in the carrier gas exiting the column. The analysis of the resulting peak allows one to determine the equilibrium constant of the adsorbate, dq/dC, at the system conditions.

Tracer pulse chromatography (TPC) is initiated by injecting an isotopically labeled sample of the carrier gas into the chromatographic system. The simplest situation in this case is to use a carrier gas consisting of the pure adsorbate of interest. An ionization cell, which detects the presence of the radioactive compound, generates a chromatographic peak similar to CPC. The ratio of the adsorbed- and gas-phase concentrations, or q/C, is obtained by analyzing this peak.

Both of the above techniques can be applied to gas mixtures containing one adsorbable component. In this case, the values of dq/dC and q/C refer to the conditions of the system, that is, the temperature and partial pressure of adsorbate in the carrier gas. By varying the partial pressure from zero to the pressure of interest, one can determine the pure gas adsorption isotherm.

Although both techniques can be applied to binary systems containing two adsorbable components, TPC data are simpler to analyze. Unfortunately, TPC also requires the injection of two isotopically labeled samples, which are sometimes expensive or difficult to obtain. Hyun and Danner (1985) developed the concentration/tracer pulse technique (C/TPC) to overcome this drawback. By injecting both a concentration and tracer pulse at various carrier gas compositions, the binary adsorption isotherms can be determined with the requirement of only one isotopically labeled sample.

Theory

The most common and simplest way to evaluate equilibrium properties from chromatographic peaks is the method of moments (Ruthven, 1984). Although this technique has deficiencies when applied to highly tailed peaks and higher-order moments, it has been proven to be quite accurate for determining the first central moments as required for the determination of equilibrium properties.

Expressions for the first moment of a chromatographic peak are determined from differential equations describing the transport process in the packed column. For CPC experiments carried out with a binary mixture of adsorbable gases and an adsorbent containing both macropores and micropores, the resulting equation is (Ruthven and Kumar, 1979):

$$t_R = t_{R,\mathrm{exp}} - t_{R,\mathrm{dead}} = \frac{L}{U}\left[1 + \left(\frac{1-\epsilon}{\epsilon}\right) \times \{\epsilon_p + (1-\epsilon_p)(y_1K_2 + y_2K_1)\}\right] \quad (1)$$

where

$$K_i = \frac{dq_i}{dC_i}$$

The corrected experimental retention time, t_R, is obtained by subtracting dead volume contributions, $t_{R,\mathrm{dead}}$, from the experimental retention time, $t_{R,\mathrm{exp}}$. The dead volume retention time is simply the system volume from the injector to the column inlet plus that from the column outlet to the detector divided by the local volumetric flow rate of the carrier gas. For a binary gas mixture containing a nonabsorbable component ($K_2 = 0$), Eq. 1 becomes:

$$t_R = \frac{L}{U}\left[1 + \left(\frac{1-\epsilon}{\epsilon}\right)\{\epsilon_p + (1-\epsilon_p)y_2K_1\}\right] \quad (2)$$

Thus, if experiments are conducted at various carrier gas flow rates, the equilibrium constant, K_1, can be obtained from the slope of a plot of t_R vs. L/U. With the definition of K_1 and assuming an ideal gas, the following equation for the amount of component i adsorbed, W_i, can be derived:

$$W_1(P_1) = \frac{q_1(P_1)}{\rho_{\mathrm{app}}} = \frac{1}{\rho_{\mathrm{app}}RT}\int_0^{P_1} K_1(P_1')\,dP_1' \quad (3)$$

This expression permits one to determine single-component isotherms from CPC experiments carried out at different carrier gas compositions.

The analysis of TPC data is simpler. For any gas mixture, the corrected retention time of an isotopically labeled pulse of component i is given by (Helfferich, 1964):

$$t_{R,i}^{*} = \frac{L}{U}\left[1 + \left(\frac{1-\epsilon}{\epsilon}\right)\{\epsilon_p + (1-\epsilon_p)K_i^{*}\}\right] \quad (4)$$

where

$$K_i^* = \frac{q_i^*}{C_i^*} = \frac{q_i}{C_i}$$

The component isotherm can be determined from rearrangement of the above expression:

$$W_i = \frac{K_i^* P_i}{\rho_{\text{app}} R T} \tag{5}$$

The C/TPC method can be used to determine binary adsorption isotherms for a mixture of two adsorbable components. In this technique, both tracer and concentration pulses are injected into a number of carrier gas mixtures of different composition and constant total pressure. In the following, we assume that an isotopically tagged sample of component 1 is available. For a given gas composition, TPC experiments are carried out at various carrier gas flow rates. The value of $K_1^*(P_1)$ is obtained from the slope of plots of $t_{R,1}^*$ vs. L/U (Eq. 4). Analysis of a range of gas compositions coupled with Eq. 5 yields a measure of the adsorption isotherm of component 1. The isotherm data are then differentiated with respect to C_1 to get K_1 of Eq. 1. Combination of this information with the CPC retention time allows one to calculate K_2 via Eq. 1. Integration of K_2 over the experimental concentration range results in the adsorption isotherm of component 2. Finally, the total adsorption isotherm is obtained by simply adding the component data.

For a single adsorbable component i at infinite dilution in an inert carrier gas, the adsorption isotherm becomes linear. Hence, the values of K_i^* and K_i become equivalent, since dq_i/dC_i equals q_i/C_i in this regime. Thus, as evidenced by Eqs. 2 and 4, the retention time of a tracer and concentration pulse becomes identical:

$$t_{R,i} = t_{R,i}^* = \frac{L}{U}\left[1 + \left(\frac{1-\epsilon}{\epsilon}\right) K_i\right] \tag{6}$$

Here, macropore terms have been dropped ($\epsilon_p \rightarrow 0$). Henry's constants, K_i, are determined from the slopes of plots of $t_{R,i}$ vs. L/U.

If the chromatographic system is operated at high interstitial gas velocities or packed with small particles, then the pressure drop across the column can become substantial. This directly affects the experimental retention time since the carrier gas is compressible. Chiang et al. (1984a) formulated the following nonisobaric first moment expression for a column packed with pure adsorbent crystals (no macropores):

$$t_{R,i} = \frac{L f_2}{U}\left[1 + \left(\frac{1-\epsilon}{\epsilon}\right) K_i\right] \tag{7}$$

where

$$f_2 = \frac{2}{3}\,\frac{\left(\dfrac{P_{\text{in}}}{P_{\text{out}}}\right)^3 - 1}{\left(\dfrac{P_{\text{in}}}{P_{\text{out}}}\right)^2 - 1} \tag{8}$$

The factor f_2 is calculated from the inlet and outlet pressures; it approaches a value of unity as $P_{\text{in}} \rightarrow P_{\text{out}}$. Thus, Henry's constants can be obtained from nonisobaric systems by plotting the corrected retention time vs. $f_2 L/U$.

Experimental Apparatus

Two chromatographic systems were used in this study—a laboratory-constructed tracer/concentration pulse apparatus containing both an ionization cell and thermal conductivity detector (IC/TCD GC) and a standard commercial gas chromatograph with a flame ionization detector (FID GC). The two systems are briefly described and compared below.

The IC/TCD GC was described in detail by Hufton and Danner (1991). The analysis was performed by integrating numerical peak data to determine the first moments. The numerical data were obtained from either an Apple IIe data acquisition computer or by digitizing strip chart recorder output.

The FID GC system consisted of a Varian 402 data acquisition computer interfaced with two independent chromatographs (Varian 6000 and 6500). An estimate of the first moment was obtained from the data acquisition computer as the time corresponding to the peak maximum ($t_{\max}$). This approximation is strictly valid only when the peaks are symmetrical, which was very nearly the case in this study. Comparison of values of $t_{\max}$ with first moments determined by numerical integration of the experimental data confirmed the validity of this simplification.

Other significant differences between the two chromatographic systems concerned regeneration and injection procedures. For the IC/TCD GC, adsorbent regeneration was carried out by heating and evacuating the column (300°C, 1-2 μm Hg). Pulses were introduced to the system via a gas injection valve. Since the FID GC apparatus did not include a vacuum pump, the adsorbent was regenerated by heating and purging with inert carrier gas (300°C, helium). Gas-tight syringes were used to inject adsorbate samples into this system.

The carrier gas flow rate in both systems was measured with soap bubble flowmeters during each run. An electronic pressure transducer was installed in both chromatographs so that the pressure drop across the packed column could be measured. Further specific details concerning both apparatuses can be found in the dissertation of Hufton (1992).

The dead volumes of both systems were determined prior to the adsorbate experiments. This was accomplished for the IC/TCD GC by pulsing sample through empty columns of various volumes and extrapolating the retention time to an effective column volume of zero. The system dead volume was calculated by multiplying this retention time by the gas volumetric flow rate. The dead volume of the FID GC system was obtained from packed-column experiments carried out with methane at 300°C. At this temperature the methane is not adsorbed to any significant extent. The dead volume of the IC/TCD GC apparatus was found to be much larger than that of the FID GC system (roughly 10 and 3 cm^3, respectively).

Characterization of the Adsorbents and Adsorbates

Silicalite, the adsorbent studied in this work, is a relatively new zeolite first described by Flanigen et al. (1978). It is structurally identical with ZSM-5, which has been extensively used in industry as a catalyst for many types of reactions (Anderson et al., 1979; Young et al., 1982). The difference between the two solids lies in the absence of exchangeable cations in silicalite. For this reason, it has been found to be less polar than most other zeolitic adsorbents (Nakamoto and Takahashi, 1982).

Unlike the more traditional faujasite zeolite, silicalite does not consist of a repeated cavity/window structure. Instead, it contains two interconnected channel networks with diameters approximately equal to 5 Å. A slightly more spacious void is created at the intersections of the two channel systems.

Two types of silicalite material were investigated in this study—small commercial crystals and large laboratory-synthesized crystals. A summary of some of the physical properties of the solids and chromatographic columns is listed in Table 1.

Table 1. Properties of Silicalite Samples and Columns

Property	Commercial Crystals: Pellets	Commercial Crystals: Pelletized Powder	Laboratory-Synthesized Crystals
Avg. Crystal Size (μm)	5×5	5×5	30×130
Crystal Shape	cubic	cubic	parallelepiped
Binder	yes	no	no
Pellet Diameter (mm)	0.45	0.45-1.2	—
Column Length (cm)	9	8-20	15
Bulk Density (g/cm^3)	1.279	1.120	—
Apparent Density (g/cm^3)	1.837	1.804	—
ϵ	0.38	~0.41	0.45-0.61
ϵ_p	0.30	0.38	—

The commercial material was obtained from Union Carbide, Tarrytown, NY, as both a powder and as extruded pellets (including binder). Each sample contained silicalite crystals that were approximately 5 μm in diameter. Hufton and Danner (1991) described the crystal powder material and outlined procedures for making binderless pellets. These and the extruded pellets were then crushed, sieved, dried, weighed and packed into 1/4-in.-dia. (6.4-mm-dia.) columns.

Large laboratory-synthesized silicalite crystals were supplied by Professor David Hayhurst, then at Cleveland State University. This material consisted of clusters of individual crystals which were roughly 30×130 μm in dimension. These crystals were packed directly into the chromatographic column—pelletization was not necessary. The large size of the particles resulted in manageable column pressure drops if lower carrier gas flow rates were used.

Helium, used as an inert carrier, was obtained as an ultra-high purity gas (>99.999%). Tracer pulse runs were carried out with a carrier gas of CP-grade ethane. Gaseous adsorbates were either CP grade (methane, ethane, and *n*-butane) or instrument grade (propane and isobutane).

A total of 2.5 mCi of ^{14}C-tagged ethane was acquired from Amersham Corporation, Arlington Heights, IL. This highly concentrated material (107 mCi/mmol) was further diluted with normal ethane to a final sample concentration of 45 mCi/mol.

Results

Henry's law constants for a range of alkanes and equilibrium isotherms of pure and binary gas mixtures on silicalite were measured via perturbation chromatography. The infinite-dilution results were measured predominantly with the FID GC; isotherm data were measured with the IC/TCD GC system.

Henry's constants

Henry's constants of methane, ethane, propane, *n*-butane and isobutane in the large laboratory-synthesized silicalite crystals were measured at various temperatures ranging between 250 and 425 K. Two sets of experiments were carried out. The first was in a 1/4-in.-dia. (6.4-mm-dia.) column connected to the IC/TCD GC. Carrier gas (helium) flow rate was maintained at a reasonable level to limit the pressure drop across the column to less than 4 kPa. Runs at higher gas velocities were investigated with the FID GC. The use of a 1/8-in.-dia. (3.2-mm-dia.) column and moderate carrier gas flow rates resulted in rather large pressure drops (up to 200 kPa). Also, the two different experimental units necessitated the utilization of different regeneration and injection procedures.

Experiments were conducted by injecting pulses of adsorbate into the helium carrier gas at various gas flow rates. The amount of adsorbate injected was varied to confirm system linearity. The value of K_i was obtained from the slope of plots of t_R vs. L/U (Eq. 6) or f_2L/U (Eq. 7). The slopes were obtained from least-squares regressions. In both sets of experiments, well-defined linear relationships were obtained from the experimental data.

Henry's constants calculated from both studies are presented in Figure 1. The general trends with increasing carbon number and temperature are as expected. Henry's constants obtained from the isobaric (IC/TCD GC) and nonisobaric (FID GC) experiments agree very well. This suggests that Eq. 7 satisfac-

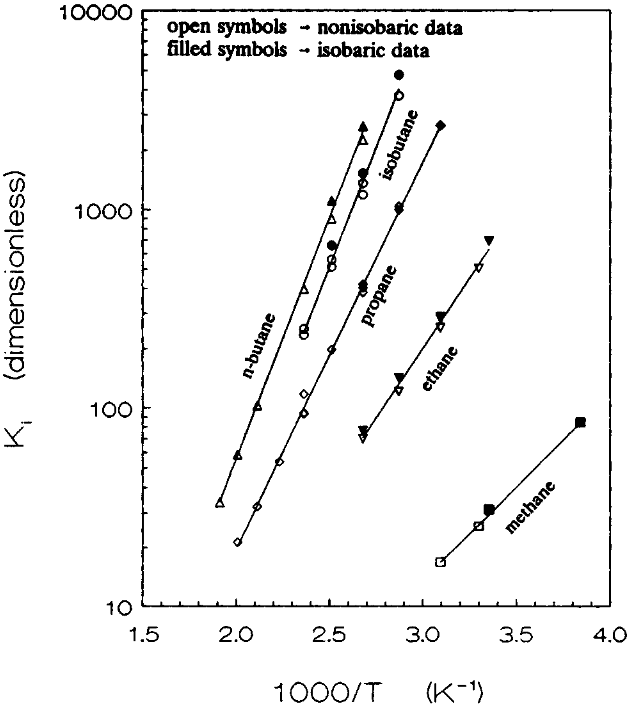

Figure 1. Henry's constants of alkanes on laboratory-synthesized silicalite as determined by CPC.

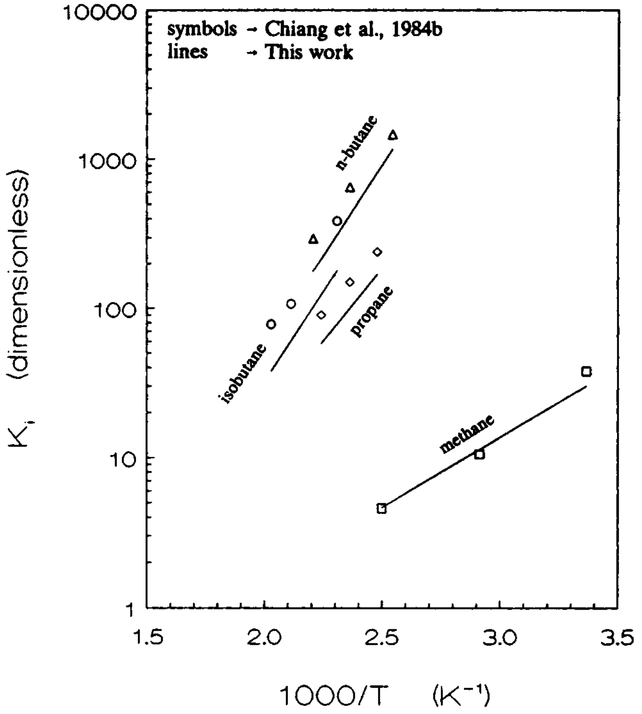

Figure 2. Comparison of Henry's constants of alkanes on laboratory-synthesized and commercial silicalite crystals.

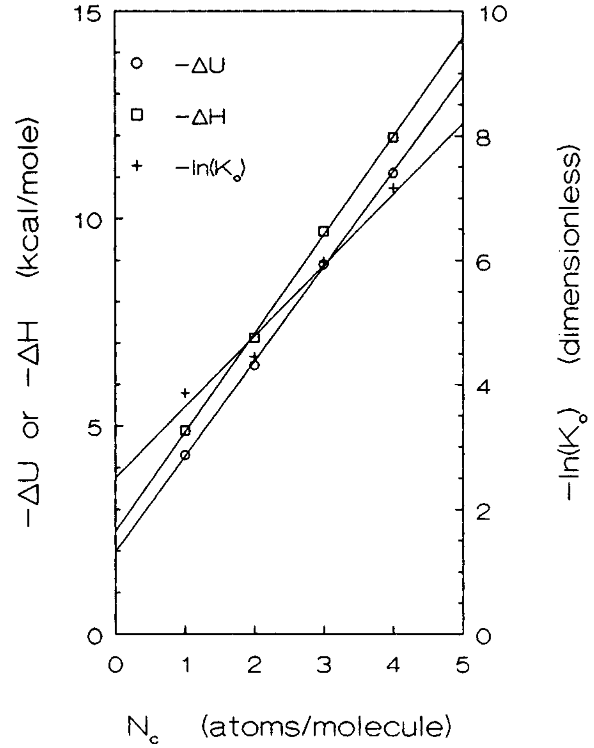

Figure 3. Effect of carbon number on $-\Delta U$, $-\Delta H$ and $-\ln(K_o)$ for linear alkanes on silicalite.

torily accounts for the experimental pressure drop and that the two different regeneration and injection methods are relatively unimportant. These data are compared with the chromatographic results of Chiang et al. (1984b) in Figure 2. They packed their column directly with the small, commercial silicalite crystals, and therefore observed very large column pressure drops (300 to 500 kPa). Reasonable agreement with their results can be taken as further support of the validity of Eq. 7. It also suggests that, as far as Henry's constants are concerned, there is no significant difference between the large laboratory-synthesized silicalite crystals and the small commercial material.

The effect of chain branching on Henry's constants can be examined on the basis of the butane data. The values of K_i for isobutane were found to be ~40% smaller than those measured for *n*-butane. This behavior is also apparent in the Chiang et al. (1984b) data. This presumably reflects the higher degree of similarity between the essentially cylindrical channels of silicalite and the rod-like shape of *n*-butane.

Table 2. Summary of Adsorption Energies for Alkanes on Silicalite

Adsorbate	$-\ln(K_o)$	$-\Delta U$ (kcal/mol)	$-\Delta H$ (kcal/mol) This Work	$-\Delta H$ (kcal/mol) Other Work
methane	3.86	4.30	4.89	5.5*
ethane	4.45	6.47	7.13	7.65**
propane	5.98	8.91	9.69	9.0*
n-butane	7.16	11.1	12.0	12.0*, 12.4**
isobutane	7.58	11.0	11.8	13.1*, 11.8**

*Chiang et al. (1984b); **Thamm (1987).

The change in internal energy with adsorption is given by the vant Hoff equation (Ruthven, 1984):

$$\ln(K) = \ln(K_o) - \frac{\Delta U}{RT} \tag{9}$$

The change in enthalpy with adsorption or the isosteric heat of adsorption can be determined from the following:

$$-\Delta H = -\Delta U + RT \tag{10}$$

Values of $\ln(K_o)$, ΔU and ΔH were determined from linear least-squares regressions of the data in Figure 1. These results are tabulated in Table 2. The heat of adsorption data agree well with other chromatographic (Chiang et al., 1984b) and calorimetric (Thamm, 1987) results. Values of $\ln(K_o)$, ΔU and ΔH for the linear alkanes are plotted vs. the number of carbon atoms in the adsorbate molecule, N_c, in Figure 3. These data were found to be reasonably linear for the adsorbates studied. The following correlations were determined by regression of the data in Figure 3:

$$\begin{aligned} -\ln(K_o) &= 1.14N_c + 2.50 \\ -\Delta U &= 2.29N_c + 1.98 \\ -\Delta H &= 2.38N_c + 2.47 \end{aligned} \tag{11}$$

where the units for ΔU and ΔH are kcal/mol. The correlation for the isosteric heat of adsorption is very similar to the equation reported by Abdul-Rehman et al. (1990).

A correlative equation for Henry's constants of linear C_1 to

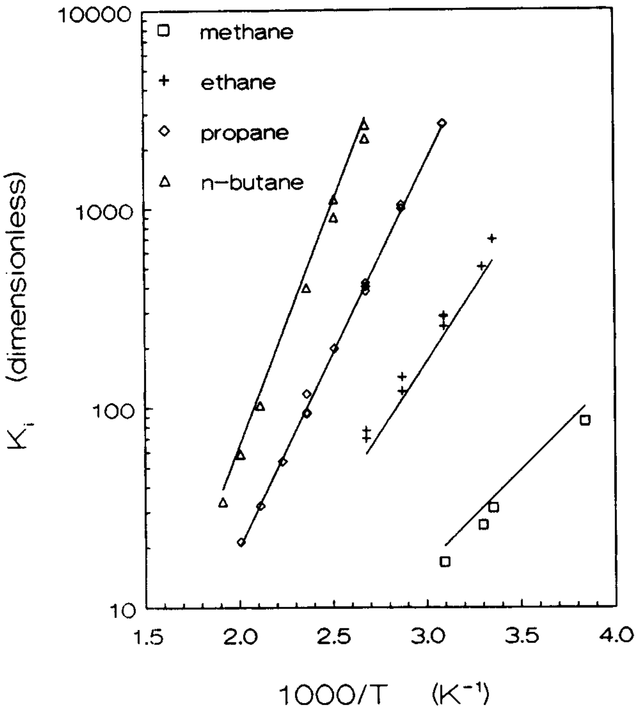

Figure 4. Comparison of experimental Henry's constants with Eq. 12: laboratory-synthesized silicalite.

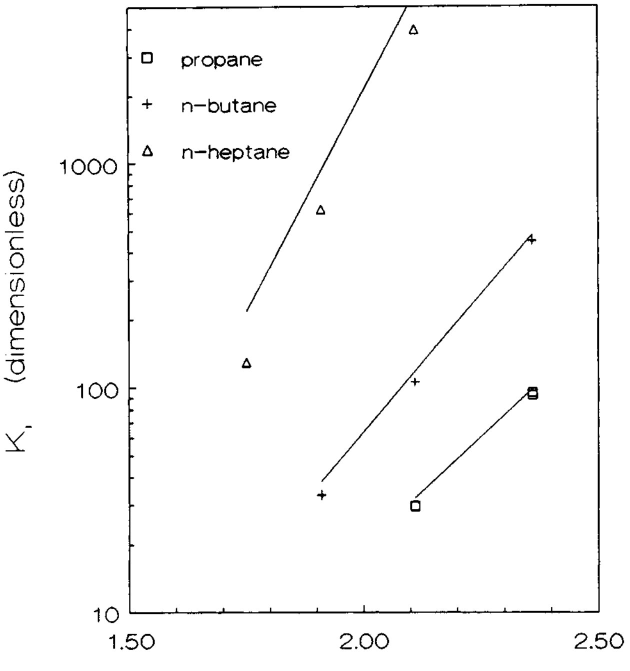

Figure 5. Comparison of Henry's constants with Eq. 12: commercial silicalite pellets.

C_4 adsorbates in silicalite can be developed by substituting the above correlations for $\ln(K_o)$ and ΔU into Eq. 9. This leads to the following result:

$$K(N_c,T) = \exp(-1.14N_c - 2.50)\exp\left(\frac{1{,}150N_c + 996}{T}\right) \qquad (12)$$

Values of K calculated from this equation are plotted along with the experimental data in Figure 4. Naturally, good agreement is observed.

The final set of experiments was carried out for propane, *n*-butane, and *n*-heptane in the commercial silicalite pellets. This adsorbent sample was an off-the-shelf product; therefore, unlike the previous materials, a binder had been added for mechanical strength. After crushing and sieving the pellets, they were placed into a 1/4-in.-dia. (6.4-mm-dia.) column and connected to the FID GC. Experiments were conducted as described above. Since macropores were present, Eq. 2 was used to determine $K(y_2 \rightarrow 1)$. The value of ϵ_p was estimated from bulk and apparent densities listed in Table 1 (determined from mercury porosimetry analysis). Henry's constants measured from these investigations are plotted in Figure 5 along with predictions from Eq. 12.

The agreement between the correlation and the propane and *n*-butane data is very good. Thus, this information plus previous conclusions based on comparisons with the Chiang et al. (1984b) data indicates that Henry's constants are insensitive to the type of silicalite material investigated. Values were found to be equivalent in commercial silicalite crystal powder and pellets, and in laboratory-synthesized crystals. The agreement between the prediction of Eq. 12 and the *n*-heptane data is reasonable considering the magnitude of the extrapolation. Thus, the validity of Eq. 12 as an approximate predictive tool for Henry's constants of linear alkanes in silicalite is supported.

Equilibrium isotherms

Hufton and Danner (1991) measured the isotherm of ethane on binderless commercial silicalite pellets at 25°C via both CPC and TPC. These results compared very well with data obtained from conventional sorption uptake experiments. The present work was directed toward the measurement of methane and carbon dioxide isotherms at 25°C on this same material. Since these two compounds were not available in isotopic form, the isotherms were determined exclusively from CPC experiments. Runs were carried out for a number of different gas mixtures containing adsorbate and helium (which was found to be nonadsorbing). Each experimental retention time, after correcting for dead volume contributions, was used to evaluate $K_1(P_1)$ from Eq. 2. These were subsequently used to define the integrand of Eq. 3. Once a sufficient number of data points had been obtained, the integral was evaluated by digitizing a best-fit curve on a plot of $K_1(P_1')$ vs. P_1' and numerically integrating the result.

Isotherms determined in this manner are presented in Figure 6 along with the previous ethane CPC data of Hufton and Danner (1991). The trend of the alkane data is expected—ethane is adsorbed much more strongly than methane at 25°C. The methane isotherm is nearly linear throughout the pressure range investigated. Carbon dioxide, like ethane, approaches saturation at adsorbate pressures of around 100 kPa, but it is not adsorbed as strongly as ethane.

Also illustrated in Figure 6 are correlations of the pure component data obtained with the Flory-Huggins vacancy solution model (FH-VSM) of Cochran et al. (1985). Computer algo-

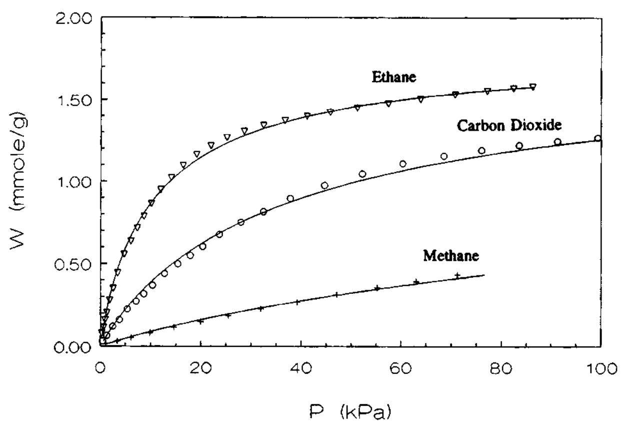

Figure 6. Pure gas isotherms of methane, ethane, and carbon dioxide on small commercial silicalite crystals as determined by CPC at 298 K.

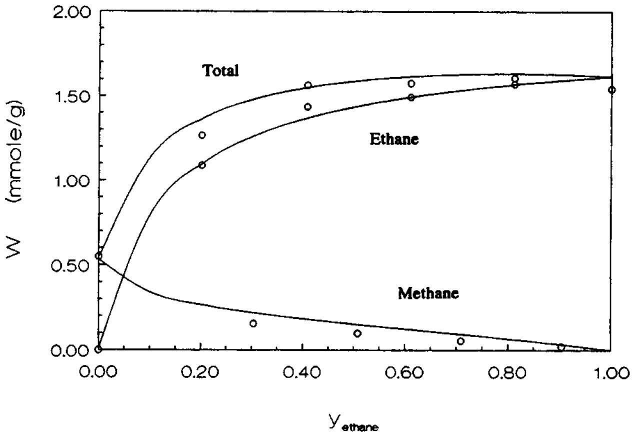

Figure 7. Binary isotherms of ethane/methane on laboratory-synthesized silicalite crystals as determined by C/TPC at 298 K.

rithm AD3 of the API Technical Data Book (Danner and Daubert, 1985) was used to conveniently regress the proper model parameters. These are listed in Table 3. (The original nomenclature of Cochran et al., 1985, has been preserved.) Figure 6 clearly indicates that this model correlates the experimental data quite well.

The next system studied was the binary methane/ethane gas mixture on laboratory-synthesized silicalite at 25°C and 107 kPa total pressure. The C/TPC technique was used to measure both component isotherms. At a given mixture composition, runs were made at various interstitial gas velocities that were low enough that nearly isobaric conditions prevailed throughout the column ($\Delta P < 4$ kPa). Pulses of ^{14}C-labeled ethane were injected into the system, thereby generating tracer and concentration pulses. Values of K^*_{ethane} were determined from the slope of plots of t^*_R vs. L/U. These allowed determination of the ethane isotherm, which was differentiated to yield values of K_{ethane}. These data were then combined with the concentration pulse retention times via Eq. 1 to evalute K_{methane}. Integration yielded a measure of the methane adsorption isotherm. The total isotherm was calculated by adding the ethane and methane contributions. The results are summarized in Figure 7. The general trends in the isotherm data are similar to those found by Abdul-Rehman et al. (1990). Ethane is the predominant species in the adsorbed phase, which is expected based on previous observations of the pure component isotherms.

Figure 7 also contains isotherm predictions of the FH-VSM based on the pure component parameters listed in Table 2. The agreement with the experimental data is good. This is not surprising since this system has both a nonpolar adsorbent and nonpolar, similar adsorbates. Other adsorption models should also give good agreement with the experimental results. With the limited data set available, however, a search for the most accurate model for alkane/silicalite systems was not justifiable.

Table 3. FH-VSM Parameters for Pure Gases on Silicalite at 298 K

Adsorbate	$10^3 \times n_i^\infty$ (mol/g)	$10^5 \times b_i$ (mol/g·kPa)	α_{iv}
CH_4	3.84	1.04	2.34
C_2H_6	1.80	22.1	0.909
CO_2	1.77	5.42	0.675

Conclusions

The linear alkane Henry's constants (C_1 to C_4) on silicalite were correlated with temperature and the number of carbon atoms in the adsorbate molecule. This correlation was successfully used to extrapolate values of K for heptane. The correlation was based on the behavior of adsorption energies, which were found to agree well with data from the literature. It may be of practical utility for the design of purification systems involving low concentrations of hydrocarbon in an inert gas stream.

Henry's constants measured from both pure crystals and pelletized material were identical if the macroporosity of the latter was taken into account. This was successfully accomplished through the analysis of mercury porosimetry results.

Both isobaric and nonisobaric chromatographic experiments yielded the same values of K_i. Thus, if infinite dilution results are desired, then it is advantageous to operate at higher flow rates since the amount of time required for elution is decreased.

The chromatographic technique made it easy to observe the effect of adsorbate branching on the equilibrium Henry's constants. The methyl branch of isobutane caused a 40% decrease in Henry's constant in comparison with n-butane. Surprisingly, the heats of adsorption of the two adsorbates were found to be essentially identical considering experimental error.

The ethane and ethane/methane isotherms measured in this study compare favorably with the results of other investigators. The FH-VSM correlated the pure gas isotherms very well and yielded a reasonable prediction of the binary ethane/methane isotherms.

Acknowledgment

This work was supported by the National Science Foundation under Grant No. CTS-9101620. We would like to thank David Hayhurst of Cleveland State University for providing the laboratory-synthesized silicalite sample and Y. H. Ma of Worcester Polytechnic University for supplying the commercial silicalite material. The experimental assistance of Heather Bergmann is also gratefully acknowledged.

Notation

b_i = Henry's law parameter of vacancy solution model, mol/g
C = gas-phase concentration, mol/cm^3
C_i = gas-phase concentration of component i, mol/cm^3
C_i^* = gas-phase concentration of tracer component i, mol/cm^3
f_2 = pressure drop correction factor, dimensionless
$-\Delta H$ = change in enthalpy upon adsorption or isosteric heat of adsorption, cal/mol
K = Henry's constant, dimensionless
K_i = equilibrium constant of component i (derivative of adsorbed-phase concentration of i with respect to gas-phase concentration of i), dimensionless
K_i^* = tracer equilibrium constant of component i (ratio of adsorbed- and gas-phase concentrations of i), dimensionless
K_o = preexponential factor of vant Hoff equation, dimensionless
L = column length, cm
n_i^∞ = saturation capacity parameter of vacancy solution model, mol/g
N_c = number of carbon atoms in a linear alkane molecule
P_i = partial pressure of component i, kPa
P_{in}, P_{out} = inlet and outlet column pressure, kPa
q_i = solid-phase concentration of component i, mol i/crystal volume, mol/cm^3
q_i^* = solid-phase concentration of tracer component i, mol labeled i/crystal volume, mol/cm^3
R = universal gas constant, 8,314.4 kPa·cm^3/mol·K
t_{max} = retention time corresponding to peak maximum, s
t_R = corrected peak retention time, s
$t_{R,dead}$ = retention time through system dead volume, s
$t_{R,exp}$ = experimental retention time through packed column, s
$t_{R,i}^*$ = corrected peak retention time of tracer component i, s
T = temperature, K
U = interstitial gas velocity evaluated at column outlet conditions, cm/s
ΔU = change in internal energy upon adsorption, cal/mol
W_i = molar amount of component i adsorbed per unit mass of adsorbent, mol/g
y_i = gas phase mole fraction of component i, dimensionless

Greek letters

α_{iv} = nonideality parameter of vacancy solution model, dimensionless
ϵ = interstitial gas volume/column volume (column porosity), dimensionless
ϵ_p = macropore volume/pellet volume (pellet porosity), dimensionless
ρ_{app} = apparent density of adsorbent, mass/crystal volume, g/cm^3

Literature Cited

Abdul-Rehman, H. B., M. A. Hasanain, and K. F. Loughlin, "Quaternary, Ternary, Binary, and Pure Component Sorption on Zeolites: 1. Light Alkanes on Linde S-115 Silicalite at Moderate to High Pressures," *Ind. Eng. Chem. Res.*, **29**, 1525 (1990).

Anderson, J. R., K. Foger, T. Mole, R. A. Rajadhyaksha, and J. V. Sanders, "Reactions on ZSM-5 Type Zeolite Catalysts," *J. Cat.*, **58**, 114 (1979).

Caro, J., M. Bülow, W. Schirmer, J. Kärger, W. Heink, H. Pfeifer, and S. P. Zdanov, "Microdynamics of Methane, Ethane, and Propane in ZSM-5 Type Zeolites," *J. Chem. Soc., Farad. Trans. I*, **81**, 2541 (1985).

Chiang, A. S., A. G. Dixon, and Y. H. Ma, "The Determination of Zeolite Crystal Diffusivity by Gas Chromatography: I. Theoretical," *Chem. Eng. Sci.*, **39**, 1451 (1984a).

Chiang, A. S., A. G. Dixon, and Y. H. Ma, "The Determination of Zeolite Crystal Diffusivity by Gas Chromatography: II. Experimental," *Chem. Eng. Sci.*, **39**, 1461 (1984b).

Cochran, T. W., R. L. Kabel, and R. P. Danner, "Vacancy Solution Theory of Adsorption using Flory-Huggins Activity Coefficient Equations," *AIChE J.*, **31**, 268 (1985).

Danner, R. P., and T. E. Daubert, "Adsorption Equilibria," *Technical Data Book—Petroleum Refining*, Chap. 15, Amer. Petrol. Inst., Washington, DC (1985).

Eic, M., and D. M. Ruthven, "Intracrystalline Diffusion of Linear Paraffins and Benzene in Silicalite Studied by the ZLC Method," *Zeolites: Facts, Figures, Future*, P. A. Jacobs and R. A. van Santen, eds., Elsevier Science Publishers, Amsterdam (1989).

Flanigen, E. M., J. M. Bennett, R. W. Grose, J. P. Cohen, R. L. Patton, A. M. Kirchner, and J. V. Smith, "Silicalite, a New Hydrophobic Crystalline Silica Molecular Sieve," *Nat.*, **271**, 512 (1978).

Hayhurst, D. T., and A. D. Paravar, "Diffusion of C_1 to C_5 Normal Paraffins in Silicalite," *Zeolites*, **8**, 27 (1988).

Helfferich, F., "Travel of Molecules and Disturbances in Chromatographic Columns, A Paradox and Its Resolution," *J. Chem. Ed.*, **41**, 410 (1964).

Hufton, J. R., "Diffusion and Equilibrium Parameters of Alkanes on Silicalite Determined by Perturbation Chromatography," PhD Diss., The Pennsylvania State Univ. (1992).

Hufton, J. R., and R. P. Danner, "Gas-Solid Diffusion and Equilibrium Parameters by Tracer Pulse Chromatography," *Chem. Eng. Sci.*, **46**, 2079 (1991).

Hyun, S. H., and R. P. Danner, "Gas Adsorption Isotherms by Use of Perturbation Chromatography," *Ind. Eng. Chem. Fundam.*, **24**, 95 (1985).

Lechert, H., and W. Schweitzer, "Gas Chromatographic Studies of Hydrocarbons in Pentasils with Different Si/Al Ratio," *Proc. Int. Conf. Zeolites*, 210 (1983).

Myers, A. L., and J. M. Prausnitz, "Thermodynamics of Mixed-Gas Adsorption," *AIChE J.*, **11**, 121 (1965).

Nakamoto, H., and H. Takahashi, "Hydrophobic Natures of Zeolite ZSM-5," *Zeolites*, **2**, 67 (1982).

Pope, C. G., "Sorption of Benzene, Toluene, and *p*-Xylene on Silicalite and H-ZSM-5," *J. Phys. Chem.*, **90**, 835 (1986).

Ruthven, D. M., *Principles of Adsorption and Adsorption Processes*, Wiley, New York (1984).

Ruthven, D. M., and R. Kumar, "A Chromatographic Study of the Diffusion of N_2, CH_4, and Binary CH_4-N_2 Mixtures in 4A Molecular Sieve," *Can. J. Chem. Eng.*, **57**, 342 (1979).

Ruthven, D. M., K. F. Loughlin, and K. A. Holborow, "Multicomponent Sorption Equilibrium in Molecular Sieve Zeolites," *Chem. Eng. Sci.*, **28**, 701 (1973).

Shah, D. B., D. T. Hayhurst, G. Evanina, and C. J. Guo, "Sorption and Diffusion of Benzene in HZSM-5 and Silicalite Crystals," *AIChE J.*, **34**, 1713 (1988).

Stach, H., H. Thamm, J. Jänchen, K. Fiedler, and W. Schirmer, "Experimental and Theoretical Investigations of the Adsorption of *n*-Paraffins, *n*-Olefins, and Aromatics on Silicalite," *Proc. Int. Conf. Zeolites*, 225 (1983).

Stach, H., U. Lohse, H. Thamm, and W. Schirmer, "Adsorption Equilibria of Hydrocarbons on Highly Dealuminated Zeolites," *Zeolites*, **6**, 74 (1986).

Thamm, H., "Adsorption Site Heterogeneity in Silicalite: A Calorimetric Study," *Zeolites*, **7**, 341 (1987).

van den Begin, N., L. V. C. Rees, J. Caro, and M. Bülow, "Fast Adsorption-Desorption Kinetics of Hydrocarbons in Silicalite-1 by the Single-Step Frequency Response Method," *Zeolites*, **9**, 287 (1989).

Wang, J.-G., Y. Chang, Y. H. Ma, H. Li, and T. D. Tang, "Adsorption Equilibrium of Ethylene-Carbon Dioxide Mixture on Zeolite ZSM5," *Proc. Int. Conf. Zeolites*, 555 (1986).

Wu, P., A. Debebe, and Y. H. Ma, "Adsorption and Diffusion of C_6 and C_8 Hydrocarbons in Silicalite," *Zeolites*, **3**, 118 (1983).

Young, L. B., S. A. Butter, and W. W. Kaeding, "Shape Selective Reactions with Zeolite Catalysts," *J. Cat.*, **76**, 418 (1982).

Zikanova, A., M. Bülow, and H. Schlodder, "Intracrystalline Diffusion of Benzene in ZSM-5 and Silicalite," *Zeolites*, **7**, 115 (1987).

Manuscript received May 18, 1992, and revision received Dec. 18, 1992.