Adsorption Equilibria of the Light Hydrocarbon Gases on the Activated Carbon and Silica Gel

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A new method is presented for the determination of adsorption equilibria for pure components and mixtures both at high and low pressures. Isotherms for carbon dioxide, methane, ethane, propane, *i*-butane, *n*-butane, *i*-pentane, and *n*-pentane on activated carbon (Columbia grade NXC 8/10) and on silica gel (Mobil Sorbead H) at 75°, 125°, 200°, and 300°F. are given for pressures ranging from below atmospheric to 1,000 lb./sq. in. Also, adsorption equilibria data are presented for several multicomponent mixtures of the light hydrocarbon gases.

The data collected were correlated with good accuracy by use of the two-layer kinetic model developed previously by Gonzalez.

Recent installations of adsorption separation processes give evidence of the renewed interest of the petroleum and petrochemical industries in the physical adsorption of pure gases and mixtures by solid adsorbents.

Presently available is a large variety of adsorbents which vary in selectivity, durability, resistance to regeneration, to crush or fracture, bulk density, and initial cost. However, in most cases the fundamental adsorption data (adsorption isotherms) are not available. The experimental method described in this paper for the determination of pure component isotherms requires a relatively simple apparatus, which is easily operated. The data so obtained may be used in turn to predict adsorption equilibria of mixtures of the respective pure components by use of the bimolecular adsorption model proposed by Gonzalez et al. (*6*).

Several comprehensive sets of data for a variety of adsorbents are available in the literature. Ray and Box (*19*) published perhaps the most comprehensive set for the adsorption of hydrogen, carbon monoxide, nitrogen, carbon dioxide, methane, acetylene, ethylene, ethane, propylene, propane, and *n*-butane on activated carbon for temperatures ranging from 100° to 450°F. and pressures ranging from below atmospheric to 250 lb./sq. in. abs. Others (*4*, *5*, *11*, *13* to *19*) have published somewhat more limited sets of data. Several authors (*1*, *5*, *8*, *11* to *13*, *18*, *20*) have published data on the adsorption equilibria of multicomponent mixtures. However, in most instances, these data pertained to either binary or ternary gas mixtures. Of the authors cited above, only Mason and Cooke (*14*) have published data on the adsorption of mixtures composed of more than four components.

This paper presents data for the adsorption of both pure components and mixtures on two common varieties of adsorbents, activated carbon and silica gel. Adsorption isotherms were determined on a silica gel (Mobil Sorbead H) and on activated carbon (Columbia grade NXC 8/10) for carbon dioxide, methane, ethane, propane, *i*-butane, *n*-butane, *i*-pentane, and *n*-pentane at the temperatures 75°, 125°, 200°, and 300°F. and at pressures ranging from below atmospheric to 1,000 lb./sq. in.

The pure component isotherms were used in the kinetic model of Gonzalez et al. (*6*) to predict the adsorption equilibria of several multicomponent mixtures. Comparisons of the observed and predicted adsorption equilibria for nine different mixtures are presented.

A description of the equipment used to determine the adsorption equilibria for both pure components and mixtures follows.

EXPERIMENTAL APPARATUS AND PROCEDURE

The experimental apparatus used for collecting the adsorption data consisted of three different arrangements of equipment. Figure 1 shows the diagram of the equipment used for the determination of the pure component isotherms. Figure 2 shows the diagram of the experimental apparatus used to determine the equilibrium adsorptions of multicomponent mixtures by each of the two adsorbents mentioned. Figure 3 shows the arrangement employed to recover the adsorbate (composed of a multicomponent mixture) from the adsorbent.

The adsorption tubes shown in Figures 1 through 3 consisted of ¼-in. aluminum tubing either 9 in. long (used for the activated carbon adsorbent) or 12 in. long (used for the silical gel). Aluminum valves (Hoke, model 3212G4A) were used, and pure copper sponge (kitchen ware type) was used at the terminals of the tube as a packing gland. The amount of adsorbent inside the tubes

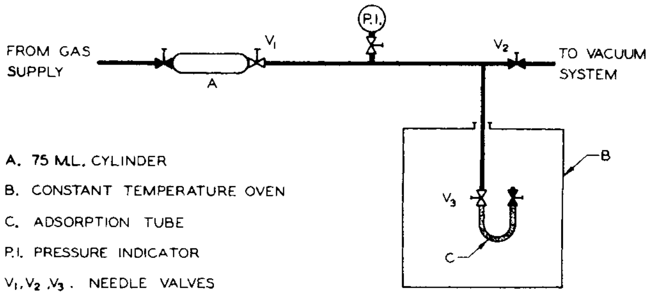

Fig. 1. Apparatus for the adsorption of pure components.

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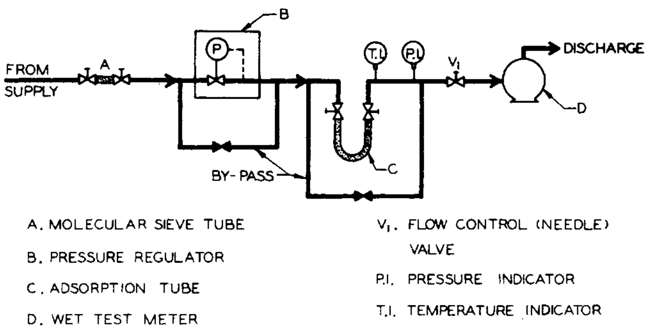

Fig. 2. Apparatus for the adsorption of multicomponent mixtures.

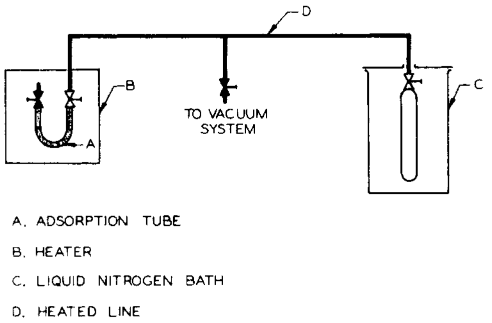

Fig. 3. Apparatus used for the desorption of the multicomponent samples.

was approximately 1.1 to 1.5 g. of carbon and 2.3 to 3.8 g. of silica gel. The amounts adsorbed ranged from a few milligrams to approximately 500 mg. The total weight of an adsorption tube filled with an adsorbent and fitted with valves ranged from approximately 77 g. for the carbon to 82 g. for a tube filled with silica gel.

The gases used were research grade. Carbon dioxide was obtained from the Matheson Company, and the hydrocarbons (methane, ethane, propane, *i*-butane, and *n*-butane) were obtained from Phillips Petroleum Company. The liquid hydrocarbons (*i*-pentane and *n*-pentane) were pure grade (99 mole % minimum purity) and were also obtained from Phillips Petroleum Company.

Some of the auxiliary pieces of equipment used consisted of an electric oven (Thelco Model 29), a vacuum pump, an analytical balance, a chromatographic unit, and a few other laboratory items.

Experimental Procedure

The first step in the determination of the pure component isotherm consisted of degassing the bulk adsorbent. After the adsorbent had been heated to 500°F. and flushed several times with high purity helium, it was evacuated at 500°F. for about 12 hr. Then it was transferred to an adsorption tube, connected to the system, and evacuated for 2 hr. at 300°F. After the adsorption system, including cylinder *A* had been evacuated, valve v_2 was closed, the system was pressurized with the gas whose isotherm was to be determined, and then the adsorption system was isolated from the supply source by closing the valve preceding cylinder *A* of Figure 1. The capacitance of cylinder *A* helped to maintain the pressure constant throughout a given equilibrium determination. After the given gas had been allowed to contact the adsorbent at a particular temperature and pressure for a period of time long enough to ensure equilibrium, valves v_1 and v_3 were closed, and the adsorption tube was disconnected and weighed. The first point of each isotherm was determined at the highest pressure desired. After the adsorption tube had been weighed it was reconnected to the system, and with valves v_1 and v_3 in the closed position, valve v_2 was opened in order to evacuate the tubing of the adsorption system. Then valve v_2 was closed, v_1 and v_3 opened in the order described below, and the next equilibrium point determined. Generally, for the determination of each isotherm, the adsorption system was filled only once with gas from the supply source. The procedure described was repeated until the pressure within the system was less than a prescribed lower limit. The order in which valves v_1 and v_3 were opened prior to the determination of each point was alternated from one equilibrium determination to the next. This procedure tended to force the equilibrium to be approached first from the high pressure side and then from the low pressure side. After a given isotherm had been determined, the remainder of the adsorbed gas was then removed from the adsorbent, and the procedure described above was repeated for another isotherm. It should be mentioned that for the 75°F. isotherms, a constant-temperature water bath rather than the oven was used for controlling the temperature of the adsorption tube.

The procedure for collecting the multicomponent equilibrium data consisted first of connecting the equipment shown in Figure 2 to the supply lines at the Vanderbilt Gas Plant of Mobil Oil Corporation. The gas mixture was allowed to flow through the adsorption tube for about 1.5 hr. (Approximately 1,400 liters of the mixture at about 50°F. and atmospheric pressure were passed through each tube.) The amount of gas which was passed through the adsorption tube was determined by the use of the results of previous tests on these plant streams by Mobil Oil Corporation (*10*). At least twice the amount calculated from these tests was employed.

The molecular sieve (Linde type 5A) filter shown in Figure 2 consisted of a short adsorption tube filled with approximately 0.3 g. of the molecular sieve. After each run the sieve was changed. The sieve served as a filter to remove any small solid particles that might have been in the gas stream and as an adsorbent for the removal of water vapor as well as any extraneous oil droplets that might have been in the gas stream.

Any possible effect of this filter was assumed to be negligible. Before any flow through the adsorption tube was permitted, a sufficient amount of gas was passed through the filter to saturate it with all components except water.

The total amount of the multicomponent mixture adsorbed from the gas stream was determined gravimetrically. After the adsorbed gas mixture, as well as the unadsorbed gas within the tube, had been removed by use of the equipment shown in Figure 3, the composition of the gas removed was determined with a gas chromatograph. In order to achieve complete desorption, the tube was heated in three steps while its contents were being withdrawn by means of the cold trap (the liquid nitrogen bath) shown in Figure 3.

The gas chromatographic equipment employed was a highly accurate experimental device. It consisted of a Varian Aerograph unit (model 1520) equipped with a 40-ft. column (filled with 25% d.c., 200/500, 30/60 Chromosorb P), linear temperature programmer, flame ionization and thermal conductivity detectors, and an Infotronics digital integrator model CRS-104.

In order to determine the time required to achieve (for all practical purposes) a state of equilibrium for each pure component, a number of preliminary runs were made at a variety of temperatures and pressures. These runs were also used to obtain a measure of the reproducibility of the weighing procedure. For the adsorption of light gases such as carbon dioxide and methane at intermediate pressures, the weights of the tubes checked to within a milligram. At these intermediate pressure ranges, the reproducibility of weighing was about 1%, and at the lower pressures the reproducibility of weighing was about 4%.

Generally, after several determinations (usually the set corresponding to one isotherm), the adsorption tube and its contents were discarded and a new one filled with fresh adsorbent was used to make the next set of determinations. Thus each sequence of runs was independent of any event which might have occurred in the previous set of determinations, such as the milling of the metal or the contamination of either the adsorption tube or the adsorbent.

Reduction of Experimental Data

At high pressures the weight of gas trapped in the free space inside the adsorption tube represented a significant amount relative to the weight of gas adsorbed. Thus an accurate determination of this free or dead space was needed. This dead-space was determined by use of helium which was not adsorbed to any appreciable extent by the adsorbents. This dead-space volume was used to compute the mass of gas contained in the free space in the adsorption tubes. The amount of gas adsorbed in a given experiment was computed by subtracting the mass of the gas in the dead space from the total amount of gas contained in the tube. This adjustment was made for the adsorption of both pure components and mixtures. For the pure components compressibility factors were read from the charts of Edmister (*3*). For mixtures compressibility factors were determined by use of generalized compressibility charts as described by Edmister (*3*). To use these charts, the reduced temperatures and reduced pressures for the respective mixtures were required. These quantities were computed on the basis of the corresponding molal-average-critical temperature and molal-average-critical pressure for each mixture.

No attempt was made to adjust the volume of the dead space for the relatively small volume occupied by the adsorbed phase.

Possible Sources of Experimental Error

Because of the simplicity of the experimental method employed, most of the errors could be attributed to the technique of the experimenter in the determination of the masses. These errors were involved not only in the weighings before and after each equilibrium determination, but also in the weighings required in the determination of the dead space within the adsorption tube. In addition, there always existed, of course, the possibility of leaks in the valves and fittings. In the case of the multicomponent adsorptions, difficulties were encountered at first in preventing the desorbed gas from condensing in the line connecting the adsorption tube and the cylinder immersed in the liquid nitrogen bath (see Figure 3). This problem appeared to have been solved by wrapping these connecting lines with heater elements.

Also, it should be mentioned that the temperature of the oven was more difficult to control at temperatures near ambient, such as 125°F., than at the higher temperatures. The small fluctuations in temperature which were observed in the determination of the 125°F. isotherms no doubt contributed to corresponding fluctuations of the amounts adsorbed for these isotherms.

USE OF THE KINETIC MULTILAYER MODEL FOR THE PREDICTION OF MULTICOMPONENT ADSORPTION EQUILIBRIA

Based on assumptions similar to Langmuir's (*12*), plus the added assumption that ν is the same constant for all components i

$$\nu = \frac{K_{2i}}{K_{1i}} = \frac{K_{3i}}{K_{2i}} = \cdots = \frac{K_{ni}}{K_{n-1,i}} \tag{1}$$

formulas were developed by Gonzalez et al. (*6*) for the multilayer adsorption of multicomponent mixtures. The expression so obtained for the moles of component i adsorbed (per unit mass of adsorbent) in n layers is given by

$$(C_i)_{\text{mixture}} = \left[\frac{C_T K_{1i}\bar{f}_i^{\nu}}{1+\phi_1}\right]$$

$$\left[1 + \nu\phi_1 + \nu^3\phi_1^2 + \nu^6\phi_1^3 + \nu^{10}\phi_1^4 + \cdots + \nu^{\frac{(n-1)n}{2}}\phi_1^{n-1}\right] \tag{2}$$

Each term within the second bracket of Equation (2) represents the contribution of the given layer relative to the first; that is, 1 represents the first layer, $\nu\phi_1$ the second layer, $\nu^3\phi_1^2$ the third layer, and $\nu^{\frac{(n-2)n}{2}}\phi_1^{n-1}$ the n^{th} layer.

For the data collected the contributions of the third- and higher-order layers were negligible and Equation (2) reduced to

$$C_{i_{\text{mixture}}} = C_T K_{1i}\bar{f}_i^{\nu}\left[\frac{1+\nu\sum\limits_{i=1} K_{1i}\bar{f}_i^{\nu}}{1+\sum\limits_{i=1}^{c} K_{1i}\bar{f}_i^{\nu}}\right] \tag{3}$$

For the adsorption of pure component i, this expression reduces to

$$(C_i)_{\text{pure component}} = C_T K_{1i} f_i^{\nu}\left[\frac{1+\nu K_{1i} f_i^{\nu}}{1+K_{1i} f_i^{\nu}}\right] \tag{4}$$

The variation of the parameters C_T, ν, and the K_{1i}'s in the above equations with temperature was accounted for in the curve fits by use of expressions of the form

$$C_T = c_1 e^{c_2/T} \tag{5}$$

$$K_{1i} = a_{1i} e^{a_{2i}/T} \tag{6}$$

$$\nu = b_1 e^{b_2/T} \tag{7}$$

where T is the absolute temperature.

The curve fitting of all of the pure component isotherms to Equations (4) through (7) was done simultaneously. The values for C_T and ν which gave the best curve fits for all components simultaneously were determined while a value for K_{1i} was determined for each of the respective components. Actually, these same data were curve fitted to expressions for three-layer adsorption [the terms $(1 + \nu\phi_1 + \nu^3\phi_1^2)$ appear in the second bracket of Equation (2)], and for all practical purposes the same values were obtained for the parameters for three-layer adsorption as were obtained for two-layer adsorption. The result arises from the fact that the contributions of the third- and higher-ordered layers to the total amount adsorbed were negligible. For example, the contributions of the first, second, third, and fourth layers for run 9 on silica gel (given in Table 7*) were as follows:

first layer : 1
second layer: $\nu\phi_1 \cong (0.048)(3.2) = 0.153$
third layer : $\nu^3\phi_1^2 \cong (0.048)^3(3.2)^2 = 0.00011$
fourth layer : $\nu^6\phi_1^3 \cong (0.048)^6(3.2)^3 = 0.000000004$

The parameters determined through curve fitting the pure component isotherms were then used in Equation (3) to predict equilibrium adsorptions of each component i in a multicomponent mixture. (The mixtures must of course consist of some combination of the components for which isotherms were determined.)

These same parameters also appear in an equation of state which was shown by Gonzalez et al. (*6*) to be in agreement both with the kinetic model for C_i [Equation (2)] and Gibbs' equation. For the adsorption of a multicomponent mixture in n layers, this expression is of the form

$$\begin{aligned}
\frac{\pi}{RT} &= C_T \sum_{j=1}^{n} \chi_j \\
\chi_1 &= \log_e(1+\phi_1) \\
\chi_2 &= -\nu\chi_1 + \nu\phi_1 \\
\chi_3 &= -\nu^2\chi_2 + \frac{\nu^3\phi_1^2}{2} \\
\chi_4 &= -\nu^3\chi_3 + \frac{\nu^6\phi_1^3}{3} \\
\chi_5 &= -\nu^{n-1}\chi_{n-1} + \frac{\nu^{10}\phi_1^4}{4} \\
&\vdots \\
\chi_n &= -\nu^{n-1}\chi_{n-1} + \frac{\nu^{\frac{(n-1)n}{2}}\phi_1^{n-1}}{n-1}
\end{aligned} \tag{8}$$

For two-layer adsorption, Equation (8) reduces to

$$\frac{\pi}{RT} = C_T\{\log_e(1+\phi_1) + \nu[\phi_1 - \log_e(1+\phi_1)]\} \tag{9}$$

Since this expression is thermodynamically consistent, it may be used with the appropriate thermodynamic relationships to predict other physical quantities of the adsorbed phase. Of particular significance is the fact that it can be shown that mixtures whose adsorptions can be represented by the kinetic model form ideal solutions.

Equations (2), (3), (4), (8), and (9) are based on the assumption that the amount of adsorption in all layers ($n \geq 2$) is small relative to the adsorption in the first layer as implied by Equation (9) of reference *6*. When this approximation is replaced by the more general statement of the form

$$C_{S_1} = C_{1A} + C_{1B} - C_{2A} - C_{2B} \tag{10}$$

for each adsorbed layer and for any number of components, the expression obtained for the adsorption of component i in n layers is

$$C_i = C_T K_{1i} \bar{f}_i^V \left[\frac{\Omega_{n-1}}{\prod_{j=0}^{n-1} (1 + \nu^j \phi_1)} \right] \tag{11}$$

where

$$\Omega_0 = 1$$

$$\Omega_{n-1} = \Omega_{n-2}(1 + \nu^{n-1}\phi_1) + \nu^{\frac{(n-1)n}{2}} \phi_1^{n-1}, \quad (n \geqq 2)$$

Thus, for $n = 2$,

$$C_i = C_T K_{1i} \bar{f}_i^V \left[\frac{1}{1 + \phi_1} + \frac{\nu\phi_1}{(1 + \phi_1)(1 + \nu\phi_1)} \right]$$

and for small values of $\nu\phi_1$ relative unity, this expression reduces to Equation (3).

Also, for the general case indicated by Equation (10), the expression, instead of Equation (8), obtained for the equation of state, is

$$\frac{\pi}{RT} = C_T^\sigma \int_0^{\phi_1} \frac{\Omega_{n-1}\, d\phi_1}{\prod_{j=0}^{n-1} (1 + \nu^j \phi_1)} \tag{12}$$

DISCUSSION OF RESULTS

The experimental isotherms for the adsorption of carbon dioxide, methane, ethane, propane, *i*-butane, *n*-butane, *i*-pentane, and *n*-pentane at temperatures ranging from 75° and 300°F. and pressures ranging from below atmospheric to 1,000 lb./sq. in. on activated carbon (Columbia grade NXC 8/10 and on silica gel (Mobil Sorbead H) are presented in Tables 4* and 5.* The physical properties, such as the densities, pore volumes, and surface areas, are presented in Table 6.* For each adsorbent, the parameters C_T, ν, and the K_{1i}'s were determined by curve fitting simultaneously the isotherms of the pure components to Equations (4), (5), (6), and (7). Table 1 gives the values of the parameters so obtained for activated carbon and Table 2 the values for silica gel. Typical of the results is the comparison shown in Figure 4 of the experimental adsorptions and curve fits for methane. Fugacities for the pure components which appear in Equation (4) were taken from the charts presented by Edmister (*3*). The overall standard deviation for all of the pure component data for the silica gel was 0.012 and 0.029 for all of the pure component data for activated carbon.

Because of the relatively low vapor pressure of normal hexane, its adsorption isotherms could not be determined with the desired precision by use of the apparatus described, and its adsorption constant K_1 was approximated by extrapolation as shown in Figure 5. These extrapolated values of K_1 were curve fitted to Equation (6) and the values of the parameters a_1 and a_2 so determined appear in Tables 1 and 2.

The parameters given in Tables 1 and 2 were then used in Equation (3) to predict the multicomponent adsorptions corresponding to the nine experimental observations, four of which are given in Table 3. The results of the remaining observations are available elsewhere in Table 7.* In the calculation of the predicted adsorptions, the K_1 for *n*-hexane was used for the experimentally observed hexane + fraction. Fugacities for the components in the gas-

TABLE 1. PARAMETERS FROM THE CURVE FITTING OF THE ADSORPTION DATA FOR ACTIVATED CARBON TO EQUATIONS (4), (5), (6), (7)

	$K_{1i} = a_{1i} \exp(a_{2i}/T)$	T, °R.
Component	a_{1i}	a_{2i}
Carbon dioxide	0.2598×10^{-4}	0.3818×10^4
Methane	0.1596×10^{-2}	0.1082×10^4
Ethane	0.8056×10^{-2}	0.1510×10^4
Propane	0.3859×10^{-2}	0.2507×10^4
i-Butane	0.2811×10^{-2}	0.2803×10^4
n-Butane	0.8108×10^{-3}	0.4130×10^4
i-Pentane	0.1294×10^{-1}	0.2577×10^4
n-Pentane	0.3133×10^{-2}	0.3852×10^4
n-Hexane*	0.9000×10^{-3}	0.5220×10^4

$C_T = (0.06864) \exp(1151/T)$, T is in °R.
$\nu = (0.002516) \exp(51.06/T)$, T is in °R.

Note: Use pressure units of lb./sq. in. abs. to obtain lb.-moles adsorbed per 100 lb. of adsorbent.

*Estimated as shown in Figure 2.

TABLE 2. PARAMETERS FROM THE CURVE FITTING OF THE ADSORPTION DATA FOR SILICA GEL TO EQUATIONS (4), (5), (6), (7)

	$K_{1i} = a_{1i} \exp(a_{2i}/T)$	T, °R.
Component	a_{1i}	T, °R.
Carbon dioxide	0.2386×10^{-3}	0.1879×10^4
Methane	0.2481×10^{-4}	0.1778×10^4
Ethane	0.1012×10^{-3}	0.1883×10^4
Propane	0.3367×10^{-4}	0.3317×10^4
i-Butane	0.3505×10^{-3}	0.2522×10^4
n-Butane	0.8426×10^{-4}	0.3630×10^4
i-Pentane	0.1759×10^{-3}	0.3708×10^4
n-Pentane	0.2805×10^{-3}	0.3583×10^4
n-Hexane*	0.5000×10^{-3}	0.4060×10^4

$C_T = (0.06558) \exp(1166/T)$, T is in °R.
$\nu = (0.005013) \exp(1256/T)$, T is in °R.

Note: Use pressure units of lb./sq. in. abs. to obtain lb.-moles adsorbed per 100 lb. of adsorbent.

*Estimated in the way as shown for activated carbon.

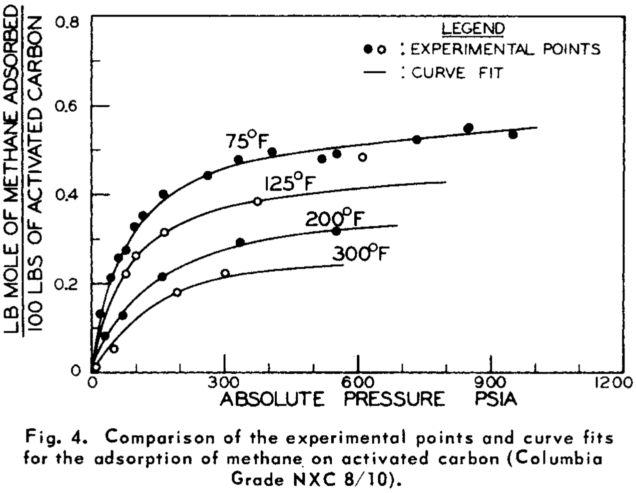

Fig. 4. Comparison of the experimental points and curve fits for the adsorption of methane on activated carbon (Columbia Grade NXC 8/10).

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*Tables 4 through 7 were deposited as document 01321 with the ASIS National Auxiliary Publications Service, c/o CCM Information Sciences, Inc., 22 W. 34th St., New York 10001 and may be obtained for \$2.00 for microfiche or \$6.50 for photocopies.

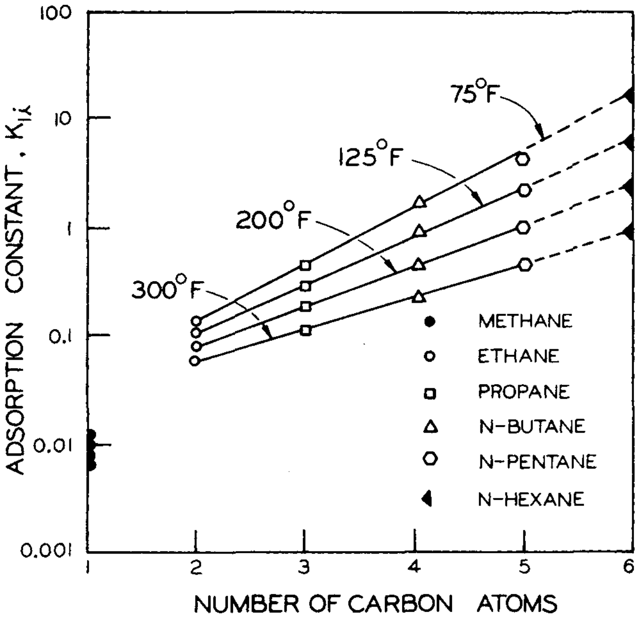

Fig. 5. Prediction of the adsorption constant K_1 for *n*-hexane by extrapolation from the adsorption constants K_{1i} for *n*-pentane and lighter components on activated carbon (Columbia Grade NXC 8/10).

TABLE 3. ADSORPTION EQUILIBRIA OF MULTICOMPONENT MIXTURES RUNS 2, 3, 5, AND 6

	Run 2 on activated carbon Temperature, 82°F. Pressure, 225 lb./sq. in. abs.				Run 3 on activated carbon Temperature, 94°F. Pressure, 995 lb./sq. in. abs.			
		lb.-mole ads. per 100 lbs.				lb.-mole ads. per 100 lbs.		
Component	y_i	Calc.	Exp.	Dev.	y_i	Calc.	Exp.	Dev.
Methane	0.9538	0.140	0.131	0.009	0.9263	0.123	0.107	0.160
Ethane	0.0296	0.047	0.048	−0.001	0.0364	0.038	0.041	−0.003
Propane	0.0078	0.034	0.030	0.004	0.0138	0.035	0.034	0.001
i-Butane	0.0028	0.015	0.015	0.000	0.0047	0.012	0.012	0.000
n-Butane	0.0022	0.033	0.037	0.001	0.0039	0.030	0.029	0.001
i-Pentane	0.0013	0.019	0.017	0.002	0.0024	0.014	0.014	0.000
n-Pentane	0.0007	0.026	0.028	−0.002	0.0020	0.027	0.029	−0.002
Hexane	0.0018	0.222	0.242	−0.020	0.0105	0.324	0.375	−0.051
	Run 5 on silica gel Temperature, 82°F. Pressure, 255 lb./sq. in. abs.				Run 6 on silica gel Temperature, 96°F. Pressure, 945 lb./sq. in. abs.			
		lb.-mole ads. per 100 lbs.				lb.-mole ads. per 100 lbs.		
Component	y_i	Calc.	Exp.	Dev.	y_i	Calc.	Exp.	Dev.
Methane	0.9538	0.056	0.058	−0.002	0.9524	0.143	0.166	−0.023
Ethane	0.0296	0.008	0.007	0.001	0.0316	0.017	0.017	0.000
Propane	0.0078	0.009	0.009	0.000	0.0085	0.017	0.017	0.000
i-Butane	0.0028	0.008	0.008	−0.000	0.0028	0.011	0.010	0.001
n-Butane	0.0022	0.011	0.010	0.001	0.0021	0.014	0.015	−0.001
i-Pentane	0.0013	0.015	0.015	0.000	0.0011	0.014	0.017	0.001
n-Pentane	0.0007	0.010	0.009	0.001	0.0007	0.011	0.010	0.001
Hexane	0.0018	0.103	0.131	−0.028	0.0008	0.040	0.039	0.001

eous mixture were approximated by use of the P-T-C *K* charts of Edmister (*3*).

To test the statistical reliability of the correlation for mixtures, the chi-square test was used. The value of chi-square calculated for the combined effect of all five runs on silica gel was 0.023 and 0.030 for the combined effect of all four runs on actived carbon.

The largest deviations of the experimental points from the curve fit for each isotherm generally occurred at the lowest pressures (*7*), where the experimental error was also the greatest.

It should be pointed out, however, that if the experimental data for each individual component had been separately curve fitted, different values for C_T and ν would have been obtained because of the experimental deviations of the data and, perhaps more importantly, because C_T reflects the molal area (or the number of adsorption sites) that the adsorbent presents to a given component. Since certain sites such as those within small pores may be available to small molecules but not to large molecules, the quantity C_T obviously depends upon both the identity of the component as well as the adsorbent. However, the variation of C_T for a given adsorbent was not great enough to prevent the obtaining of a good correlation when the data for all components were curve fit simultaneously. The curve fitting procedure has the effect of averaging C_T over all components of the set simultaneously. Similarily, any component dependency which ν may possess is likewise averaged over all components by the curve fitting procedure. Results such as those shown in Figure 5 suggest that the kinetic model can be expected to work best for families of similar substances. Thus extreme care should be taken in the use of the values of the parameters C_T, ν, and K_{1i} for a component in one system to predict its relative behavior in another. Although carbon dioxide does not belong to the hydrocarbon family investigated, the curve fits for the carbon dioxide data were about as good as those for the hydrocarbons (*7*).

CONCLUSIONS

The technique employed for obtaining adsorption isotherms for pure components is simple, and its accuracy is generally within the reproducibility of an adsorbent. Also, it was demonstrated that the continuous flow methods could be used to obtain adsorption equilibrium data for multicomponent mixtures. This method (*2*, *4*, *8*) had been used in the past primarily for the adsorption of binary mixtures.

The two-layer adsorption model proposed by Gonzalez et al. (*6*) was further tested and shown to be a satisfactory method for representing the equilibrium adsorptions of multicomponent mixtures of the light hydrocarbon gases. Also, the effect of temperature and pressure on the adsorption of pure components as well as multicomponent mixtures is adequately represented by the model.

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NOTATION

a_{1i}, a_{2i} = constants in the expression for the adsorption equilibrium constant in Equation (6)
b_1, b_2 = constants in the expression for ν as given by Equation (7)
c_1, c_2 = constants in the expression for C_T as given by Equation (5)
$(C_i)_{\text{mixture}}$ = lb.-moles of component i adsorbed from a mixture of gases per 100 lb. of adsorbent

$(C_i)_{\text{pure component}}$ = lb.-moles of component i adsorbed in the presence of pure component i in the gas phase per 100 lb. adsorbent

C_T = parameter in Equation (2), total lb.-moles of adsorption sites per 100 lb. of adsorbent; C_T^{σ} has the same meaning except that it is based on a unit of adsorption surface area rather than 100 lb. of adsorbent

$\overline{f}_i^v$ = fugacity of component i in a mixture of vapors, lb./sq. in. abs.

f_i^v = fugacity of pure component i, lb./sq. in. abs.

K_{ji} = adsorption equilibrium constant for pure component i in layer j (see reference *6*)

ν = parameter as defined by Equation (1); see also reference *6*

$\phi = \sum_{i=1}^{c} K_{1i}\overline{f}_i^V$, where $\overline{f}_i^V$ is the fugacity of component i in the gas phase at the conditions of the experiment.

Subscripts

c = total number of component in a given mixture

i = component number, $(1 \leq i \leq c)$

j = number of layers, $(1 \leq j \leq n)$

n = total number of adsorbed layers

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Polymerization in a Tubular Reactor

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A mathematical model has been developed to predict the variations in temperature, velocity, and composition which occur during anionic polymerization in laminar flow in a tubular reactor. It is found that very large radial gradients in all three are to be expected when a solution containing only solvent and monomer is polymerized. Recycle of part of the product or prepolymerization in stirred-tank reactors may be used to reduce greatly the distortion of the radial profiles.

The concept of the tubular reactor for polymerization, in which monomer enters at one end (either pure or in a solvent) and leaves as polymer at the other end, is attractive because of its simplicity and potential low cost. Marring this picture is the tendency for polymer to form a thick layer on the tube wall, reducing the capacity of the reactor or even rendering it unworkable. It is therefore of interest to be able to predict the conditions under which operation