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Adsorption of Hydrocarbon Gas Mixtures at High Pressure

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An experimental investigation was made of the adsorption on silica gel of components from light hydrocarbon mixtures, and the results were used to test a multicomponent adsorption theory. Experimental methods included a volumetric technique to measure pure component adsorption and flow techniques for adsorption from mixtures. Although the majority of measurements was made at 100°F., two mixtures were studied over the temperature range 40° to 160°F. Pressure was varied up to 1,800 lb./sq.in.abs. The Brunauer-Emmett-Teller (BET) theory of adsorption, as extended to mixtures by Hill, was tested against the experimental data and was found to be adequate for calculating adsorption from hydrocarbon mixtures of components heavier than methane. To account for nonideal behavior, the fugacity of each component in the gas and in the adsorbed phases was calculated by using the Benedict-Webb-Rubin equation of state. The differences in experimental and theoretical values for adsorption capacity were less than 10% for most of the conditions tested, but ranged up to about 25% for the highest pressures studied. Although the BET theory represents a simplified model of a complex process, it can be used to supply adsorption data for engineering application over ranges of pressure, temperature, and gas composition usually encountered in adsorption processing of natural gas mixtures.

The increasing use of adsorption separation techniques in the natural gas industry generates a need for basic data essential to effective design of adsorption processing equipment. Gas streams processed in adsorption plants usually contain about 90% or more of methane, with the remainder consisting of higher molecular weight paraffin hydrocarbons. Pressures commonly range from 300 to 1,200 lb./sq.in.abs. and temperatures from 80° to 120°F. Equilibrium adsorption capacities of commonly used adsorbents for the individual components of these complex, high-pressure, natural gas systems are therefore needed for a wide range of conditions.

Literature references to adsorption data for multicomponent natural gas mixtures are very scarce. Lewis et al. (*1*) and Gilmer and Kobayashi (*2*) published the only available information on adsorption of hydrocarbon gas mixtures on silica gel at pressures greater than atmospheric. However, all these results are limited to data for five binary mixtures. Most of the measurements were made at pressures less than those usually encountered in the field.

The investigation described in this paper was designed to supply experimental data concerning the adsorption capacity of individual components from natural gas mixtures on silica gel, one of the most commonly used adsorbents in the natural gas industry. Effects of pressure, gas composition, and, to a lesser extent, temperature were investigated over ranges encompassing those usually encountered in natural gas treating. Applicability of various adsorption theories to the resulting data was also investigated.

In the succeeding paragraphs, results of the adsorption capacity experiments are presented, and a multicomponent adsorption theory, capable of reproducing the experimental data within limits of accuracy acceptable for design purposes, is described.

ADSORPTION THEORY

Of various theories examined for application to high-pressure multicomponent adsorption data, that by Brunauer, Emmett, and Teller (*3*) (BET) as extended to gas mixtures by Hill (*4*) was found to be most satisfactory for reproducing experimental data obtained during this investigation. This result is not unexpected, since pressures of interest are sufficiently high to cause multilayer adsorption and nonideality in the gas and adsorbed phases. The Langmuir theory and the Polanyi potential theory, as applied by Lewis et al. (*1*), were found to be inadequate. In the following sections, application of the BET theory to pure gases and of Hill's modified BET theory to gas mixtures is discussed. For those interested in a general review and comparison of adsorption theories, publications by Young and Crowell (*5*) and by Adamson (*6*) are recommended.

Adsorption of Pure Materials

The BET theory for single-component adsorption is based on a model in which a different behavior is assumed for the first and for successive adsorbed layers. The theory has been developed from kinetic theory and from statistical mechanics (*5*). In the model used, molecules in the first layer are attracted to the surface by the short-range forces of the solid. The second and higher layers are assumed to behave as vapor-liquid systems. Thus, the heat associated with attachment of the first layer to the adsorbent surface is the heat of adsorption and that of higher layers is equal to the heat of liquefaction. In the original BET theory (used here), heat of adsorption is assumed to be independent of amount adsorbed (*7*). One form of the equation for the adsorption isotherm is

$$\frac{p}{\bar{n}(p^\circ - p)} = \frac{1}{\bar{n}_m c} + \frac{c-1}{\bar{n}_m c}\left(\frac{p}{p^\circ}\right) \qquad (1)$$

Equation (1) was derived for pressure ranges where the materials behave as ideal gases. To account for nonideal behavior over more extensive pressure ranges used in the present work, a derivation was made in which fugacities replaced pressures.

A problem encountered in the use of Equation (1) to describe adsorption of the components of natural gas mixtures is that the temperatures of interest are above the critical temperatures for methane and ethane. To circumvent this problem, pseudo values of p° were obtained for these two materials from the extrapolated plots of saturation vapor pressure vs. temperature given by Maxwell (*8*). This approach permitted satisfactory application of the BET theory to the heavier components in natural gas mixtures.

Adsorption from Gas Mixtures

The theory for mixture adsorption developed by Hill (*4*) is based on a similar model to the single-component BET theory. Deviations from ideal mixtures are considered in the liquid layers (second and higher) and the energy of attachment of a molecule in the i^{th} layer is assumed to depend upon the composition of only the $(i-1)^{\text{th}}$ layer. Adsorption for any number of layers can be calculated. The amount of adsorption predicted decreases for layers increasing in distance from the surface.

Calculations were made in the present study for two and three layers of adsorbate. However, results and equations are shown only for two. For the mixtures and experimental conditions used, the fugacity of each component was far below that for the saturated vapor. For these conditions, the amount of adsorbed material drops off sharply with successive layers away from the adsorbent surface. The predicted adsorption for two layers usually was not more than 25% greater than that for one layer, and that for three layers only a few percent greater than that for two. In addition, the small pore diameter, 22 Å., of the silica gel used precludes adsorption of more than two or three layers.

The equation used in the present work for two-layer adsorption is

$$\frac{\bar{n}_j}{\bar{n}_{mj}} = \frac{E_0\left[(1+E_1)\,\gamma_{j1} + E_1\,\gamma_{j2}\right]}{1 + E_0\,(1+E_1)} \qquad (2)$$

where

$$E_0 = \sum_{j=1}^{n} x_j c_j \qquad (2a)$$

$$x_j = f_j/f_j^\circ \qquad (2b)$$

$$E_1 = \sum_{j=1}^{n} x_j F_j(N_{j1}) \qquad (2c)$$

$$F_j(N_{j1}) = N_{j1} f_j^\circ / f_{Lj1} \qquad (2d)$$

$$N_{j1} = x_j c_j / E_0 \qquad (2e)$$

$$\gamma_{ji} = \frac{N_{ji}}{N_{1i}\left[\frac{A_1}{A_j}\right] + N_{2i}\left[\frac{A_2}{A_j}\right] + \ldots + N_{ji} + \ldots N_{ni}\left[\frac{A_n}{A_j}\right]} \qquad (2f)$$

$$N_{j2} = x_j F_j(N_{j1}) / E_1 \qquad (2g)$$

Equations (2*a*) through (2*g*) are those shown by Hill, except for the use of fugacity instead of pressure.

By Hill's model, effects of nonideal solution behavior on composition of the adsorbed phase are accounted for by $F(N)$ of Equation (2*c*). This term reflects the difference in the heat of liquefaction, at system temperature, of a molecule condensing into a liquid of the composition of the $(i-1)^{\text{th}}$ adsorbed layer and into a single component of the same species. $F(N)$, as defined by Hill, is the reciprocal of the correction necessary when applying the Lewis and Randall fugacity rule to liquid systems exhibiting nonideal solution behavior. The f_{Lji} in Equation (2*d*) is the fugacity of the j^{th} component in a liquid of the composition of the $(i-1)^{\text{th}}$ adsorbed layer N_{ji-1}; the liquid is at its bubble point and system temperature. For the work reported here, the Benedict-Webb-Rubin (B-W-R) equation of state (*9*) and thermodynamic relations of fugacities to PVT data were used to compute the required f_{Lji}'s.

The f_{Lji} of Equation (2*d*) is not defined for cases in which system temperature is above the critical temperature of a fluid of the composition of the adsorbed phase. In this paper, the adsorbed phase of such systems is assumed to be an ideal solution requiring $F(N)$ to be equal to one and removing the need for calculating f_L.

As a practical matter, the fugacity of a fluid phase, whether it be liquid or gaseous, of the composition of the adsorbed phase at the temperature and pressure of the adsorption system may be used to calculate $F(N)$ for all systems studied experimentally in the present work. For systems below critical temperature of the adsorbed phase, the calculated results with fugacities used at system pressure and temperature closely approximated those which used bubble point fugacities. For systems with no bubble point at system temperature, the results which used fugacities at system conditions calculated from the B-W-R equation were actually closer to experimental values than when ideal solutions were assumed. This agreement may be fortuitous.

To apply Equation (2) the amount and composition of the surface layer are first calculated. Then, if necessary, $F(N)$ can be calculated and used to compute adsorption in the second layer. Calculations are best made with a computer. A step-by-step procedure for use of Equation (2) is given in the Appendix.

EXPERIMENTAL PROCEDURES

To cover the range of variables studied, three experimental techniques were used to measure adsorption: a static volumetric method and two flow methods.

Volumetric Method

In the volumetric method for measuring adsorption capacity, a weighed adsorbent sample is contacted in a closed system with a gas of known composition. The system volume and quantity of gas must be known. After adsorption equilibrium is reached, the pressure, composition, and temperature are used to calculate the quantity of each component remaining in the gaseous phase. The amount of each component adsorbed can then be calculated.

The procedure for preparing the adsorbent and measuring the void volume of the system included heating the adsorbent to 500°F. for 3 hr. and cooling it in a desiccator. After this treatment, approximately 50 g. of adsorbent were placed in the cell, and the temperature was raised to 500°F. while a vacuum was applied until the pressure was less than 10μ Hg. To measure the void volume, a known quantity of helium was metered into the system and the pressure was measured. Pressures ranged from 400 to 700 lb./sq.in.; to avoid errors from helium adsorption, temperatures above 400°F. were used. Void volume of the system was calculated from PVT data for helium. After the volume measurement, the system was evacuated and brought to temperature for an adsorption experiment.

For an adsorption measurement, a sample of gas was injected with either a gas burette or a mercury injection pump as the pressure required. The system was allowed to equilibrate, and the pressure and temperature were recorded. For mixtures, a rocker-arm type of mercury pump (*1*) was used to circulate the gas during equilibration.

For single-component gases, the system volume, temperature, and pressure, and the PVT data of Sage and Lacey (*10*) were used in a mass balance to calculate equilibrium adsorption. For gas mixtures, chromatographic analyses of the injected gas and the equilibrium gas supplemented PVT data. From the analyses and a calculation of the quantity of gas mixture present, based on PVT data, a mass balance determined the adsorption of each component.

At 100°F. and at pressures above 200 lb./sq.in.abs., the volume of the adsorbed phase affects adsorption calculated. In the volumetric data reported for pure methane, ethane, and the binary mixture with methane, it was assumed that adsorbate density equalled liquid density of the material at the atmospheric pressure boiling point. Taking into account the volume of the adsorbed phase in this way increased the calculated adsorption of methane and ethane, and converted the values to absolute adsorption (11). (Adsorption of pure methane and pure ethane will be shown, both including and neglecting the adsorbed phase volume.) The volumetric method was used for measuring all single-component data. Also, since it was the only one of the three techniques used that permitted measurement of adsorption of *every* component in a multicomponent gas system, it also was used in the study of adsorption of methane-pentane mixtures. The adsorption of methane as well as that of pentane was measured.

Flow Methods

The flow methods are based on a material balance as materials are transported by a carrier gas through an adsorbent-packed column. The inlet composition is constant during a measurement—carrier gas plus materials to be adsorbed for an adsorption measurement, or pure carrier gas for a desorption measurement. Chromatographic analysis of the effluent gas from the column and knowledge of the gas flow rate permit a material balance to be made.

The experimental apparatus used for the flow experiments includes a gas supply system which delivers a constant composition mixture to a column at a steady rate. Mixtures are prepared by injecting hydrocarbon liquids into the methane carrier upstream from the column. Flow rates are always adjusted to an actual gas velocity of 0.5 ft./sec. or less in the 0.5-in. by 42-in. column normally used. A relatively fine mesh size is desirable for the desorption measurements; 40-50 mesh adsorbent particles were used for a majority of the experiments.

In a typical experiment, the column is packed with a weighed quantity of adsorbent that has been heated at 500°F. for 3 hr. After the column is purged with carrier gas and the pressure adjusted, flow is diverted to a bypass line while composition of the inlet stream is adjusted. When the desired composition has been attained, flow is diverted back through the adsorption column. Samples of effluent from the column are withdrawn periodically for analysis until the effluent composition reaches a steady value equal to that of the inlet gas. A plot of composition with time so obtained is commonly called an adsorption breakout curve. If a desorption measurement is to be made, pure carrier gas is then passed through the column until the effluent analysis shows no trace of the materials under study. A desorption breakout curve is thus obtained.

The area behind the breakout curve is proportional to the quantity of the component adsorbed at the concentration of the inlet gas and the temperature and pressure of the column. This method can be used to measure the adsorption of all components other than the carrier in any gas mixture. However, because of reequilibration between gaseous and adsorbed phases as successive adsorption fronts move through the adsorbent bed, the column must be saturated with the most highly adsorbed material before the breakout curve for any component is complete.

For binary mixtures, values of adsorption for the heavier component at all levels of concentration up to that of the mixture used can be calculated from one desorption breakout curve. Eberly (*12*) has shown how the desorption curve can be used to make these calculations. The theory assumes instantaneous equilibrium between gaseous and adsorbed phases and absence of longitudinal diffusion in the adsorbent column. The calculation is accomplished for a concentration shown as point B in Figure 1 by integrating the area ABDC under the desorption curve. The quantity of material represented by this area equals that which would be adsorbed from a gas of the composition represented by B at the conditions of temperature and pressure in the column.

Desorption experiments were used for measuring adsorption of the heavier materials in all binary mixtures with methane. The adsorption breakout curve was used for all components heavier than methane from other gas mixtures.

Materials Used

The adsorbent used was Davison Chemical Company's O3 refrigerant grade silica gel. Surface area of the gel by nitrogen adsorption was 807 to 830 sq. meters/g. The average pore size was reported to be approximately 22Å. Particle density was 1.2 g./cc. Single-component gases used were of at least 99% purity. Ethane through *n*-hexane hydrocarbons were Phillips Petroleum Company pure grade. Methane was from a natural gas well which produces 99.9% methane, with carbon dioxide as the impurity. Gas mixtures were prepared from these single components.

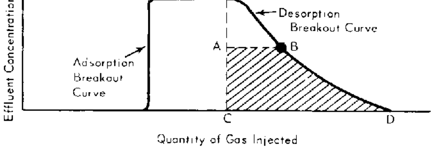

Fig. 1. Effluent gas composition from adsorption column during flow measurements of adsorption capacity.

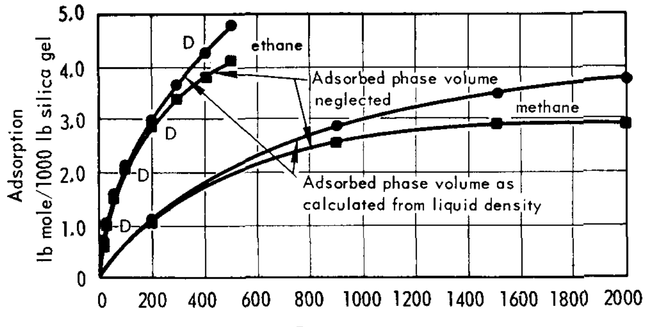

Fig. 2. Adsorption of pure hydrocarbons (methane and ethane) on silica gel at 100°F.

EXPERIMENTAL RESULTS AND COMPARISON WITH THEORY

Adsorption measurements were made by using the pure materials and a variety of mixtures. The pressure range of the mixtures was 300 to 1,800 lb./sq.in. Most of the measurements were made at a temperature of 100°F. but two mixtures were studied at temperatures from 40° to 160°F. Comparisons of pure component results with those of other investigators and comparisons of experimental multicomponent adsorption results with those calculated from Equation (2) are presented.

Pure Components

Adsorption isotherms measured at 100°F. for pure components are shown in Figures 2 and 3. Data for methane and ethane are shown with and without correction for adsorbed phase volume as discussed above. The correction is less than 10% at pressures below 300 lb./sq.in. for ethane and 800 lb./sq.in. for methane. Data obtained for pure propane, *n*-butane, iso-butane, and *n*-pentane agreed with the generalized correlation curve of Lewis et al. (*1*) for pure paraffin hydrocarbons on silica gel. This correlation is based on the Polanyi potential theory. The data for pure components did not fit the form of a Langmuir adsorption isotherm.

To obtain values of the BET constants c and n_m, adsorption data were replotted as $f/n(f^\circ - F)$ vs. f/f_o. This plot gave straight lines for values of f/f_o between approximately 0.05 to 0.3 for each hydrocarbon, and the constants were calculated from the slope and intercept of these lines. Results of the calculations are shown in Table 1. Also shown in the table are the values of the heat of adsorption ΔH_A, calculated from the value of the constant c, and the area per molecule in a complete monolayer, calculated from n_m and the nitrogen surface area of the adsorbent. The latter two values for *n*-butane and *n*-pentane agree well with those reported by Kiselev (*13*) Kiselev noted a linear increase of heat of adsorption with increasing molecular weight of the normal paraffin hydrocarbons from butane to octane; the present results confirm the observation.

Table 1. Single-Component Adsorption Constants at 100°F.

Component	c	$\bar{n}_m$, lb.-mole/ 1,000 lb. silica gel	f°, lb./sq. in. abs.	A, sq. Å./ molecule	$\Delta H_{ads.}$, g.-cal./ g.-mole
Methane	10.7	2.75	3,926*	50.1	1,475
Ethane	7.3	2.69	503*	51.2	1,235
Propane	7.7	2.70	152	51.0	4,540
i-Butane	9.2	2.47	65.6	55.8	5,705
n-Butane	11.3	2.39	47.2	57.6	6,275
i-Pentane	10.1*	2.23*	19.8	63.2*	6,900*
n-Pentane	12.1	2.18	14.7	63.2	7,650
n-Hexane	12.3*	1.97*	4.9	68.8*	9,050*

* Values obtained by extrapolation or interpolation of experimental data.

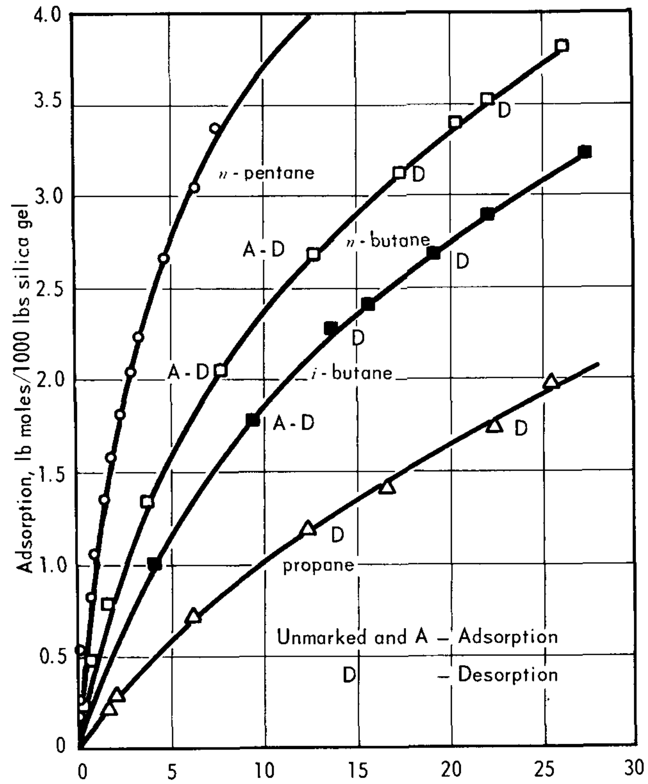

Fig. 3. Adsorption of pure hydrocarbons (pentane, butane, and propane) on silica gel at 100°F.

The calculated heats of adsorption for methane and ethane are much lower than those for the other materials. Anomalous behavior should perhaps be expected since these components were above their critical temperature. However, this behavior could also reflect uncertainty in the adsorbed phase density correction or in the experimental results at higher pressures. Results for propane appear consistent with those for the heavier components and follow the trend of linear increase with molecular weight.

Adsorption of Mixtures

The effect of additional components in a gas mixture on adsorption of a particular component can be pronounced. This effect for *n*-pentane is illustrated by the data shown in Figure 4. Temperature was maintained at 100°F. in all experiments shown here, and the partial pressure of *n*-pentane was held at 1.8 ± 0.05 lb./sq.in.abs. Pentane adsorption decreases with addition of other components. Calculations showed that most of the decrease in pentane adsorption was caused by competition between components for the available surface area, although a part of the reduction was caused by a decrease in pentane fugacity. Also shown in the figure are the amounts of pentane adsorption calculated with Equation (2) for each system. Agreement between experimental and calculated results is good.

The effect of concentration on the adsorption of one component from a binary mixture is shown in Figure 5. This graph shows the experimental and calculated variation of adsorption of *n*-butane, *n*-pentane, and *n*-hexane from mixtures of each with methane. Temperature and

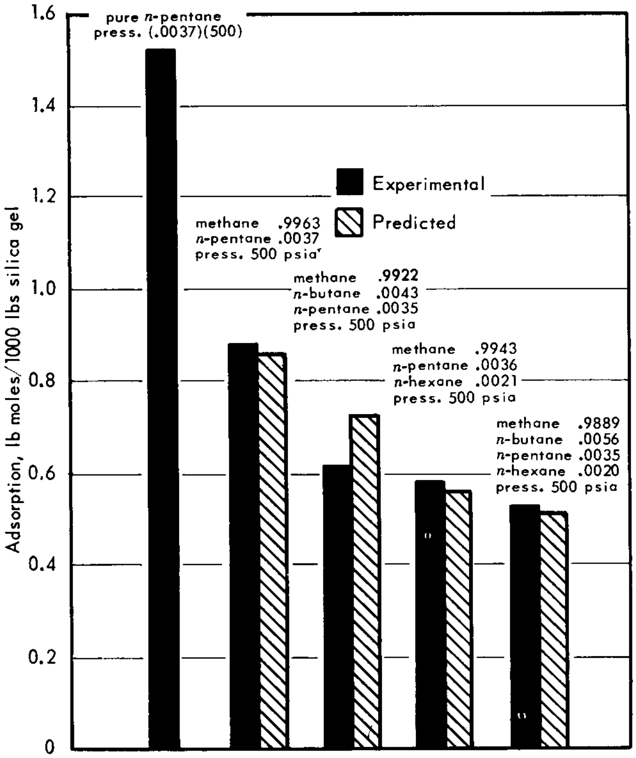

Fig. 4. Effect of added components on adsorption of *n*-pentane on silica gel at 100°F.

pressure are constant. Note that the shapes of these curves are similar to single-component isotherms. Also, the amount of adsorption increases with increasing molecular weight. The calculated curves agree within a few percent with experimental values.

As the amount of *n*-pentane or *n*-hexane adsorbed in the first layer increases, the critical temperature of the adsorbed mixture increases. When critical temperature of the mixture was below system temperature, the calculation of adsorption was made by assuming both ideal solution behavior and by using a nonideal solution correction for the second absorbed layer. The effect of using nonideal solution factors $[F(N)$ not equal $1.0]$ is shown in Figure 5 at *n*-pentane concentrations above 0.005 mole fraction. The two methods of calculation in this case bracket experimental points. For *n*-hexane, calculated adsorption with the nonideal solution factor used differs only slightly from the ideal solution calculation, as indicated by the small discontinuity in the curve at 0.002 mole fraction concentration. Nonideal solution calculations are shown above this concentration and ideal solution calculations below. For n-butane, the calculated composition of the adsorbed first layer had a critical temperature above system temperature at all concentrations used.

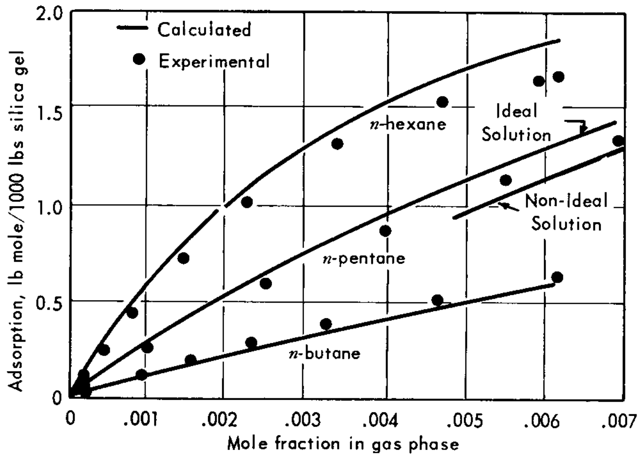

Fig. 5. Effect of concentration on silica gel adsorption of the heavier component from binary gas mixtures. (Lighter component in mixture is methane; 100°F. at 1,000 lb./sq.in.abs.)

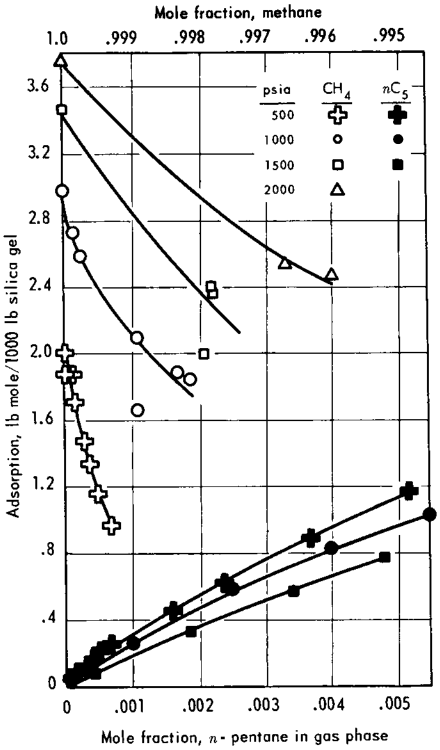

Fig. 6. Effects of pressure and composition on silica gel adsorption of both components from methane–*n*-pentane mixtures at 100°F.

Measured effects of concentration and pressure on adsorption of methane and pentane from a binary mixture are shown in Figure 6. The results show decreasing adsorption of methane with increasing pentane adsorption at each system pressure. Although calculated values are not shown, values for pentane agree with experimental results with approximately the same accuracy as the comparisons in Figure 5. As was to be expected, since the mixture temperature was above the critical for methane, calculated values for methane adsorption did not match the experimental.

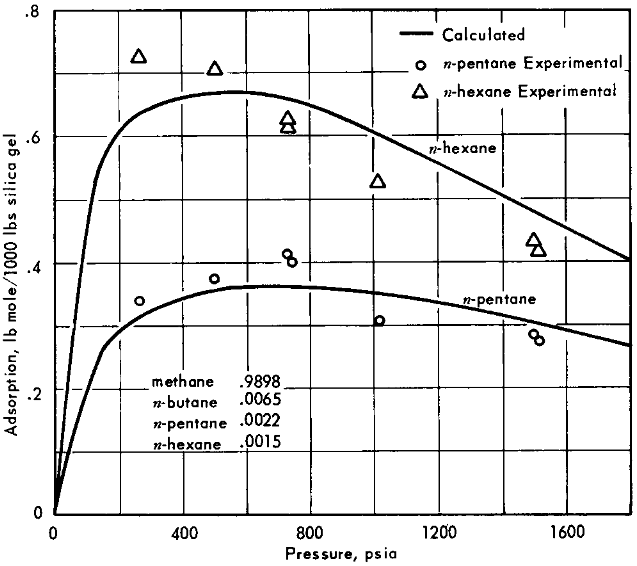

Fig. 7. Effect of total pressure on silica gel adsorption of *n*-pentane and *n*-hexane from a complex gas mixture at 100°F.

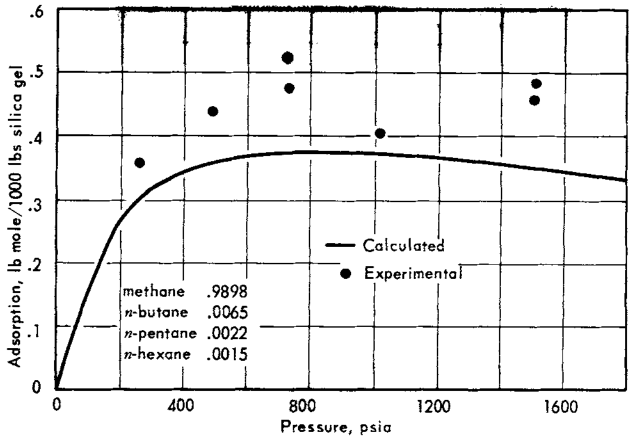

Fig. 8. Effect of total pressure on silica gel adsorption of *n*-butane from a complex gas mixture at 100°F.

Effect of total pressure on multicomponent adsorption is illustrated in Figures 7 and 8. These plots show the adsorption of *n*-hexane, *n*-pentane, and *n*-butane from a mixture of these materials with methane. The adsorption capacities for the three heavier materials were measured as the gas composition and the system temperature were held constant and the system pressure was varied. The amount of each of the three heavier materials adsorbed first rises with increasing pressure, then passes through a maximum value, and finally declines. An analogy might be drawn between this phenomenon and retrograde behavior in vapor-liquid systems.

Maxima in adsorption isotherms of the heavier components from hydrocarbon gas mixtures reflect increasing methane adsorption and decreasing gas phase fugacity of other components with increasing pressure. At high pressures the fugacity of the heavier components rises much slower with pressure than does the fugacity of methane. Fugacities of the components shown in Figures 7 and 8 actually decrease with increasing pressure at the highest pressures. Methane fugacity does not exhibit this behavior; consequently, methane is increasingly competitive for available surface area. The result is a significant decrease in adsorption of heavier components at high pressure.

Agreement of calculated and experimental values in Figures 7 and 8 is better for hexane and pentane than for butane. In general, agreement for the heavier components of a mixture was better than for lighter components of that mixture. Adsorption of butane from a mixture not containing heavier components, such as shown in Figure 9, was calculated to be nearer experimental values than the agreement shown in Figure 8.

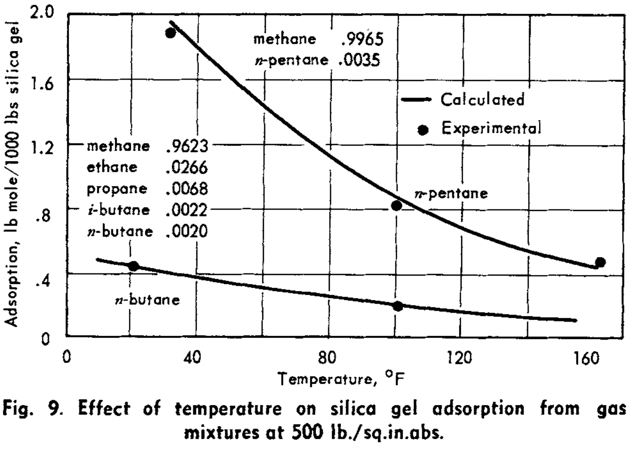

Fig. 9. Effect of temperature on silica gel adsorption from gas mixtures at 500 lb./sq.in.abs.

Table 2. Experimental and Predicted Adsorption of Complex Gas Mixtures on Silica Gel at 100°F.

Mixture A, P = 1,400 lb./sq. in. abs.

Component	Concentration	$\bar{n}$ Exp.	$\bar{n}$ Calculated	% Deviation
Methane	0.9184			
Ethane	0.0400			
Propane	0.0240	0.335	0.322	−4
i-Butane	0.0068	0.274	0.192	−30
n-Butane	0.0056	0.235	0.235	0
i-Pentane	0.0020	0.187	0.144	−23
n-Pentane	0.0012	0.136	0.125	−8
n-Hexane	0.0020	0.516	0.480	−7

Mixture B, P = 1,000 lb./sq. in. abs.

Component	Concentration	$\bar{n}$ Exp.	$\bar{n}$ Calculated	% Deviation
Methane	0.9747			
Ethane	0.0151			
Propane	0.0067	0.146	0.126	−14
i-Butane				
n-Butane	0.0012	0.065	0.081	+24
i-Pentane				
n-Pentane	0.0012	0.191	0.226	+18
n-Hexane	0.0012	0.491	0.542	+10

Effect of temperature on adsorption of a heavier component from gas mixtures is illustrated in Figure 9. Data are given for the adsorption of *n*-butane from a mixture composed of five materials and of *n*-pentane from a two-component mixture. In each case, the amount of adsorption decreases with increasing temperature. As would be expected from BET theory, the effect is much more pronounced for the *n*-pentane in the two-component mixture.

Adsorption data for complex gas mixtures are given in Table 2. A comparison of predicted and experimental adsorption for the propane through hexane components of two complex gas mixtures is included in the table. For mixture A deviations between calculated and experimental values range from 0 to 30%. For mixture B deviations range from 10 to 24%. The experimental accuracy of these data is not as great as for simpler systems. Measurements for the lighter hydrocarbons are particularly subject to experimental error and these errors contribute substantially to the deviations between calculated and experimental results.

Adsorption from a mixture of ethane and propane is illustrated in Figure 10. The experimental data are from a paper of Lewis et al. (*1*). These published data were used to test the BET theory for mixtures outside the range of experiments in the present work. Because of different silica gel used by Lewis et al., BET constants determined from their single-component data were used in Equation (2) to calculate the mixture adsorption curve in Figure 10. The agreement between theory and experimental results for both components is satisfactory.

CONCLUSIONS

Adsorption on silica gel of individual paraffin hydrocarbons, propane to hexane, from dilute gas mixtures containing more than 90 mole % methane decreases with the addition of other heavy hydrocarbons, increases with concentration of the particular component, and decreases with temperature. In addition to these expected trends, adsorption of the heavier components was found to increase, to pass through a maximum value, and then to decrease with increasing pressure. Conclusions drawn from examination of the data are:

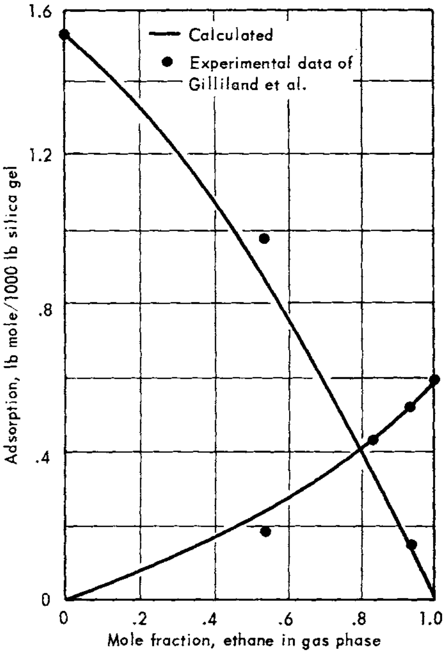

Fig. 10. Adsorption of ethane-propane gas mixtures on silica gel at 1 atm. and 25°F.

1. Adsorption on silica gel of pure hydrocarbon gases from methane through pentane can be described by the Brunauer-Emmett-Teller (BET) theory of adsorption.

2. Hill's extension of BET theory predicts adsorption on silica gel of intermediate hydrocarbons, C_3 through C_6, from natural gas mixtures with engineering accuracy for ranges of conditions commonly encountered in adsorption processing of natural gas.

NOTATION

A_j = adsorbed area per mole of component j
c_j = pure component BET energy constant for component j
E_i = ratio of adsorption surfaces s_{i+1}/s_i ($i = 0, 1, 2, \ldots.$)
f_j = gas phase fugacity of component j, lb./sq.in.abs.
f_{Lj} = fugacity of component j in reference liquid phase, lb./sq.in.abs.
f_j° = fugacity corresponding to the saturation vapor pressure of component j, lb./sq.in.abs.
$\bar{n}_j$ = adsorption of component j, lb.-mole/1,000 lb. adsorbent
$\bar{n}_{mj}$ = monolayer adsorption of component j, lb.-mole/1,000 lb. adsorbent
N_j = adsorbed phase concentration of component j
p_j = partial pressure of component j
p_j° = saturation vapor pressure of component j
p = total system pressure
q_A = heat of adsorption of pure component
q_L = heat of liquefaction of pure component
R = gas constant
s_i = adsorbed surface covered by i layers
T = system temperature, °F.
V = molar volume
x_j = relative fugacity, $(f/f^\circ)_j$
γ_{ji} = surface fraction of layer i that is covered by component j

Subscripts

i = layer of adsorption (1, 2, 3, etc., except as subscript to E)
j = number of component
n = dummy indices used in definition of γ

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APPENDIX

Calculation Procedure

The calculation procedure for the assumption of two-layer adsorption involves the following steps:

1. By using the temperature, pressure, and gas phase analysis, calculate the gas phase fugacity for every hydrocarbon component in the gas mixture with either the Polyco data charts (*14*), the Edmister and Ruby charts (*15*), or the BWR equation.

2. Calculate the fugacity ratio x_j for each component in the gas mixture by using the fugacities obtained in the preceding step and the appropriate values of f° read from Table 1 or obtained from Maxwell (*8*).

3. Calculate the product x_j and c_j for each component by using the *x's* calculated in step 2 and the appropriate *c's* from Table 1 (*c's* for temperatures other than 100°F. may be calculated by the defining equation). With these products, calculate E_O and then the N_{jl} for each component from Equation (2*a*) and (2*e*), respectively.

4. Calculate the $F_j(N_{jl})$ terms by using Equation (2*d*) when values other than one are used. The adsorbed phase fugacity f_{Ljl} is assumed to be equal to the fugacity at the temperature and pressure of the system and at the first layer composition N_{jl}. When calculating adsorption of components heavier than butane from dilute mixtures with methane, the value of the $F_j(N_{jl})$ can be taken as unity with approximately 10% loss of accuracy.

5. With the values of x_j calculated in step 2 and the values of $F_j(N_{jl})$ calculated in step 4, calculate the E_1 and the N_{j2} by Equations (2*c*) and (2*g*), as was done in step 3 for the first layer.

6. With the first layer concentration (N_{jl}), calculate the values for the γ_{jl} by Equation (2*f*). The monolayer adsorption $\bar{n}_m$ is given in Table 1 for each component at 100°F. For other temperatures, assume n_m is inversely proportional to absolute temperature.

7. Calculate the values for the γ_{j2} by using the second-layer concentrations (N_{j2}) by Equation (2*f*), as was done for the first layer.

8. Use these values with Equation (2) to calculate the adsorption of each component.

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