Adsorption on Microporous Barriers

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Adsorbed or condensed flow of gases and vapors permeating through microporous media has been linked to the adsorptive properties of the barrier (*3*, *6*, *7*, *9*). Recently, the barrier separation of gas mixtures of carbon dioxide and propane was described strictly on the basis of adsorbed flow (*10*). In this system, separation due to diffusive molecular flow should have been essentially nil, because the molecular weights of these gases (or vapors) are almost identical.

Barrier separation could become of more practical interest if the differences in adsorption behavior of gas or vapor mixtures were to be utilized, rather than the differences in molecular weights of the respective components. Without some knowledge about a particular system, it is impossible to state whether separative action of molecular weight differences, and of differences in adsorptive behavior will enhance or oppose each other. However, while the molecular weight relationship is fixed once the components have been chosen, the adsorption behavior can be manipulated by changing temperature and pressure. Thus, it becomes of considerable interest to develop information on adsorption of gases and vapors in barrier flow. In general, increased pressures promote the adsorbed flow and possibly magnifies differences in adsorptive behavior.

Utilizing adsorptive properties in a barrier separation process presents a continuous operational scheme. In contrast, the usual use of adsorptive media results in discontinuous off-and-on operation, or necessitates a fluidized operation with recycling of the adsorbent through a desorption stage. The term Molecular Sieves applied to both natural and synthetic zeolitic materials is a misnomer. A sieving operation implies continuity of flow resulting in product and reject streams, as in screening or a barrier separation. The so-called Molecular Sieve type materials are actually molecular traps and operate by removing or entrapping one or more of the constituents from a stream until the capacity to adsorb gases or vapors has been exhausted. In this respect, they are analogous to conventional adsorbents, such as activated carbon or silica gel.

MATERIALS AND PROPERTIES

The solid adsorbent used was Vycor porous glass, whose physical properties have been reported (*1*, *7*). The gases and vapors were hydrogen, nitrogen, argon, carbon dioxide, methane, ethene, propane, propene, *n*-butane, and 1-butene. All were obtained from the Matheson Co., Inc., except propane, which was obtained from the Phillips Petroleum Co. The gases were rated at or above 99% purity, so were not further purified.

Adsorption isotherms of a given gas or vapor were experimentally determined until the height of the manometer or the vapor pressure of an adsorbate at a given temperature made it impossible to make any more runs. The vapor pressure limitations are shown in Table I, obtained from Perry (*25*) and Jordan (*8*). A summary of the critical temperatures and pressures of the adsorbates is given in Table II (*2*, *25*).

Compressibility factors were used in the form of Amagat units as explained by Dodge (*5*). These were obtained from one source as much as possible to assure consistency, but it was necessary to draw from several sources to get the compressibility factors of all the gases and vapors:

Helium (*23*), hydrogen (*25*), nitrogen (*17*), argon (*22*), carbon dioxide (*18*), methane (*19*), ethene (*16*), propane, (*29*), propene (*20*, *21*), *n*-butane and 1-butene (*4*).

EXPERIMENTAL EQUIPMENT AND PROCEDURE

To obtain adequate accuracy in reading pressures, a long manometer was used. The volumes of equipment vessels and fittings were determined by using mercury displacement and physical measurements. Dead-space volume was obtained using helium gas and *P-V-T* data, assuming that helium would not adsorb on the porous glass at room temperature.

A diagram of the equipment is shown in Figure 1. As future experimental work is planned at elevated pressures, the equipment was constructed accordingly. The manometer consists of two legs, one a glass capillary tube 7 meters in length, and the other a sight glass about 40 cm. long connected at the bottom to a steel pipe reservoir, and at the top to an elbow leading to the high pressure side vessel. Stainless steel-to-glass seals at all such joints were made by using rubber gaskets and Epon adhesive VI from the Shell Chemical Corp. A stainless steel measuring tape, graduated in millimeters, was placed beside the tube, both up and down from the reference line, which was located about 0.5 meter above the floor. Pressures varied from 0.15 to about 9.4 atm. absolute. For the most part, isotherms were determined at 0°, 25°, and 40° C.

The procedure in developing the adsorption isotherms was moving up the curve in a "stairstep" fashion. This method has the advantage that a smooth isotherm is obtained, the data-taking is faster because it is not necessary to draw a vacuum on the samples between each reading, and it permits a closer approach to the vapor pressure of an adsorbate than if a single-charge procedure is used. However, the method has one distinct disadvantage: If a mistake is made during an observation, all the readings which follow in the series will be in error. The only way that an isotherm can be verified is to rerun the complete isotherm.

Table 1. Adsorbate Vapor Pressure Limitations under 10 Atm. (*8*, *25*)

	Atmospheres Pressure		
Gas or Vapor	0° C.	25° C.	40° C.
Propane	4.75	8.25	. . .
Propene	5.70	. . .	. . .
n-Butane	1.00	2.40	3.72
1-Butene	1.30	2.95	6.02

Almost all isotherm determinations were made with porous glass disks, which had been prepared at the same time and in the same manner by the Corning Glass Works. However, carbon dioxide and propane data were also obtained for a

Table II. Critical Constants of Adsorbates (*2*, *25*)

	T_c (°C.)	P_c, Atm. Abs.
Helium	−267.9	2.26
Hydrogen	−239.9	12.8
Nitrogen	−147.1	33.5
Argon	−122	48.0
Carbon dioxide	31.1	73.0
Methane	− 82.5	45.8
Ethene	9.7	50.9
Propane	96.8	42.0
Propene	92.3	45.0
n-Butane	153	36.0
1-Butene	146.4	39.7

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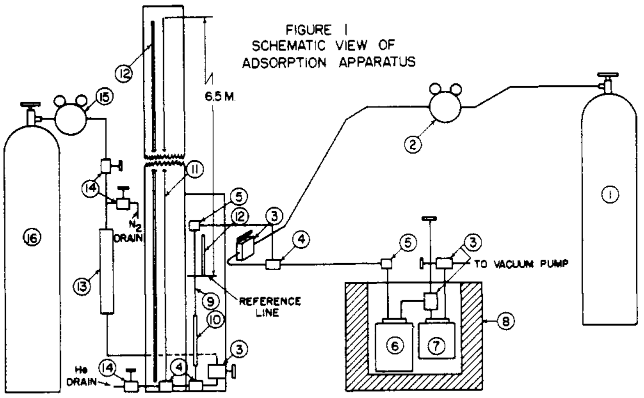


FIGURE 1 SCHEMATIC VIEW OF ADSORPTION APPARATUS

1. Test gas cylinder
2. Victor pressure regulator
3. American Instrument Co. needle valve
4. American Instrument Co. tee connector
5. American Instrument Co. elbow connector
6. American Instrument Co. high pressure vessel
7. American Instrument Co. high pressure vessel
8. Insulated constant temperature bath
9. Sight glass
10. Metal mercury reservoir
11. Glass manometer tube
12. Stainless steel measuring tape
13. Mercury pressure reservoir
14. Hoke needle valve
15. Airco pressure regulator
16. Nitrogen cylinder

porous glass thimble, similar to the barrier used in separation experiments with mixtures of these vapors (*10*). The identical barrier was not tested, because it would have been necessary to break it for the adsorption measurements.

CORRELATION OF DATA

The rather large number of data could be presented by plotting the amount adsorbed against the equilibrium adsorption pressure as isotherms for the respective temperatures; a total of ten separate plots would be required.

To establish a more generalized correlation, the Polanyi model of molecular behavior was selected as a correlating function (*26*).

The following correlations of the adsorption measurements were investigated:

Product (αv) plotted against simplified Polanyi potential $\ln (f_0/f)$

Product (αv) plotted against thermal Polanyi potential $T \ln (f_0/f)$

Product (αv) plotted against modified Polanyi potential $(T/v) \ln (f_0/f)$

where α = surface concentration, lb. mole gas adsorbed per square foot of surface area
v = specific volume of saturated liquid phase at the system pressure, cu. ft. per mole
f = fugacity of gas phase, ft. lb. force per sq. ft.
f_0 = fugacity of saturated vapor-phase, ft. lb. force per sq. ft.
T = absolute temperature, °R.

Fugacity values were calculated from the relationships given by Mathias and others (*14*), where (f/P) values can be obtained by using P and P_0 pressures, the system pressure and the vapor pressure, respectively.

Gases. Adsorption was measured for hydrogen, nitrogen, and argon at 0°, 25°, and 40° C. over a pressure range of 0.8 to 9.3 atm. absolute. All of the data could be correlated by plotting the modified Polanyi potential $(T/v) \ln (f_0/f)$ against the product, αv (Figure 2). The data are for the porous glass disk specimens. Values of v were obtained from Mathias and others (*12–14*) and vapor pressures from a United States Department of Commerce publication (*24*).

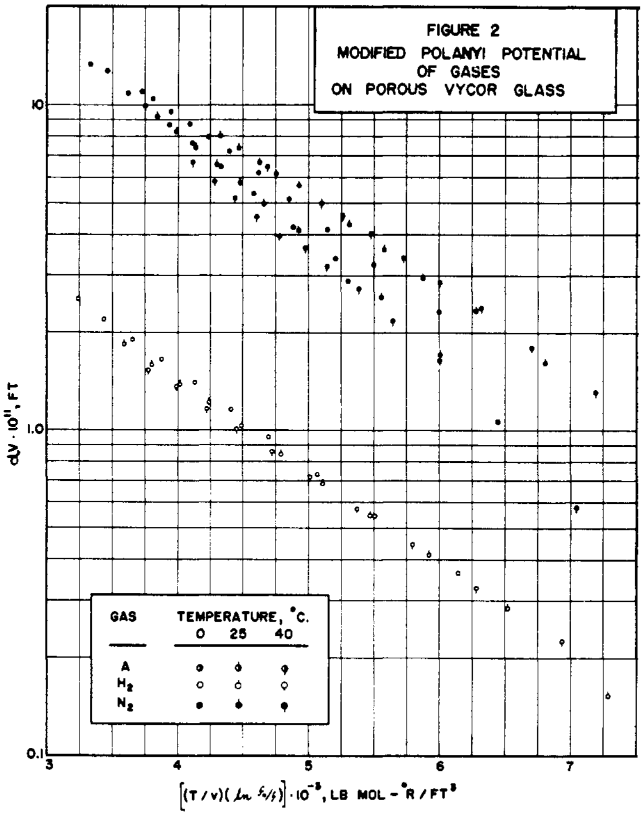


FIGURE 2 MODIFIED POLANYI POTENTIAL OF GASES ON POROUS VYCOR GLASS

Vapors. Vapor adsorption data were obtained for carbon dioxide, the alkanes methane, propane, and *n*-butane, and the alkenes ethene, propene, and 1-butene. Desorption was checked on propane, and the desorption values coincided with the adsorption data. The same temperature levels were used, and adsorption pressures varied from 0.15 to 9.3 atm. absolute, the individual ranges depending on the vapors. The alkane hydrocarbon data could be correlated satisfactorily by using either the simplified Polanyi potential or the thermal Polanyi potential function, as shown in Figures 3 and 4. The same correlations are shown in Figures 5 and 6 for the alkenes, together with the carbon dioxide data. The modified Polanyi potential function did not give any better agreement of the data. All correlations are based on adsorption data only.

The alkane data could be presented by a single curve with both types of Polanyi potentials. However, the alkene data are spread out too far to attempt correlation by any single curve.

To illustrate the utility of the correlations, the amount of vapor adsorbed is calculated for the following conditions: propane vapor at 25° C. and 4 atm. absolute.

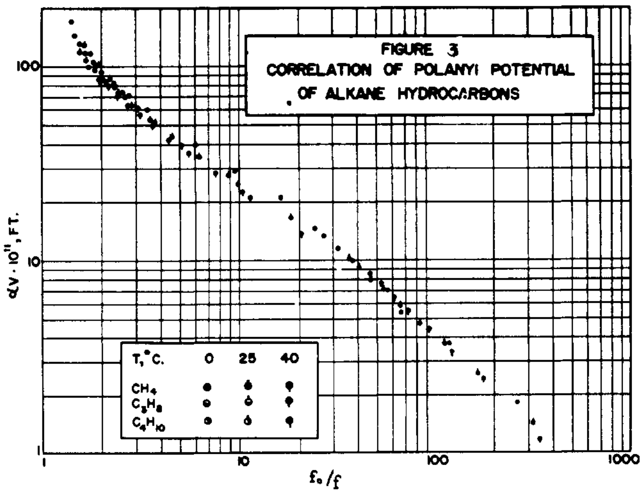


FIGURE 3 CORRELATION OF POLANYI POTENTIAL OF ALKANE HYDROCARBONS

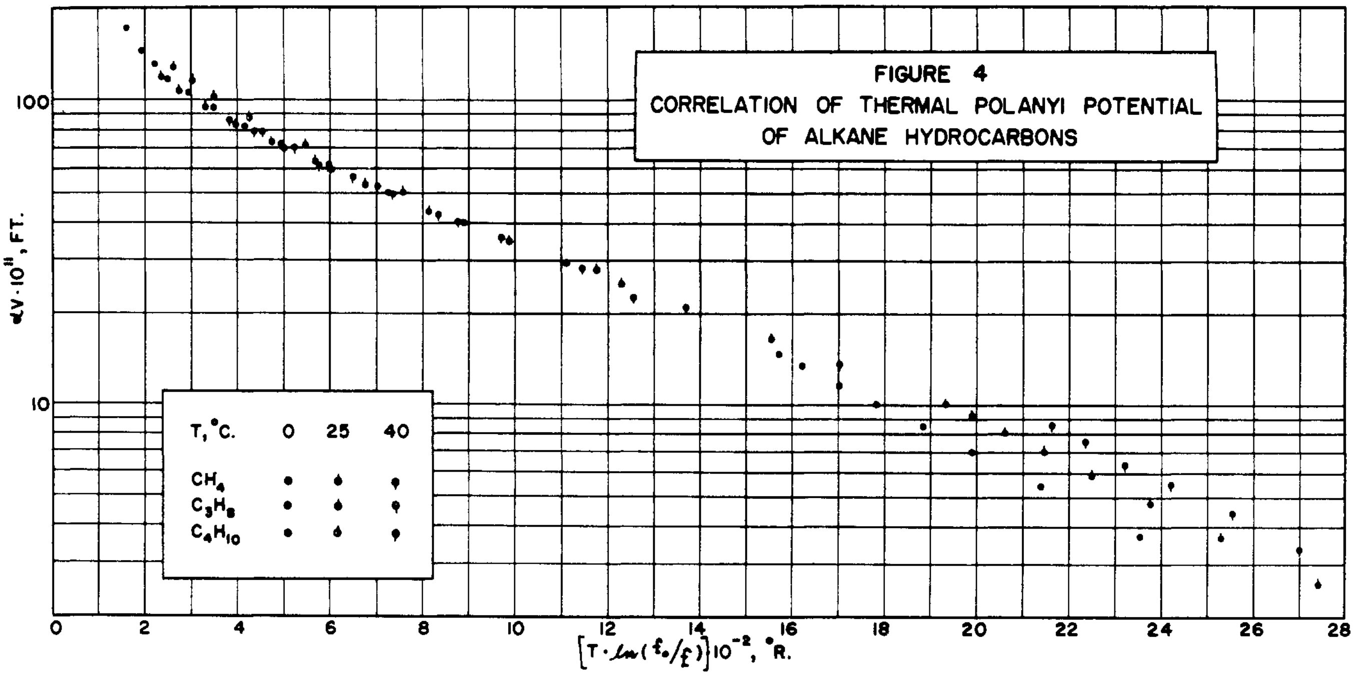


FIGURE 4
CORRELATION OF THERMAL POLANYI POTENTIAL OF ALKANE HYDROCARBONS

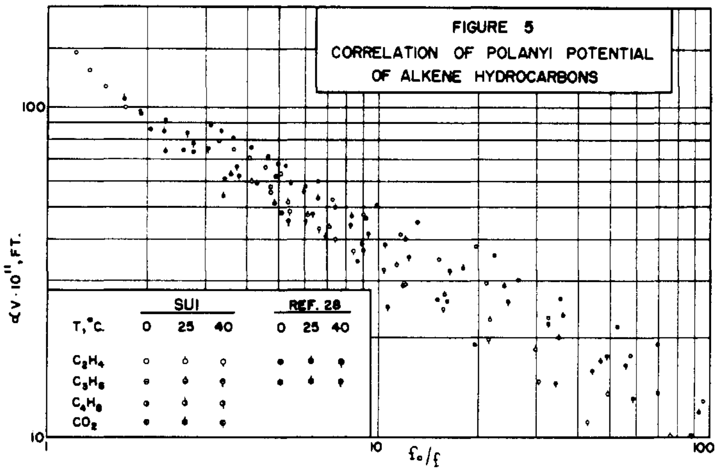


FIGURE 5
CORRELATION OF POLANYI POTENTIAL OF ALKENE HYDROCARBONS

$$
\begin{aligned}
\text{Thus: } P &= 4.0 \text{ atm.}\\
P_0 &= 9.2 \text{ atm. from } (\mathit{15})\\
P_{\text{crit.}} &= 42.0 \text{ atm. from Table II}\\
T_{\text{crit.}} &= 206.2^{\circ}\text{ F. from Table II}\\
\text{Reduced pressure, } P_r &= 4.0/42.0 = 0.0955\\
P_{or} &= 9.2/42.0 = 0.22\\
\text{Reduced temperature } T_r &= (77 + 460)/(206 + 460) = 0.805
\end{aligned}
$$

Then: $f/P = 0.93$ and $f_0/P_0 = 0.84$ from (*15*, p. 62)

Therefore: $f_0/f = 2.07$, and from Figure 3: $(\alpha v)10^{11} = 83.5$.

The molal specific volume of the liquid phase, v, is to be evaluated at the equilibrium adsorption pressure, 4.0 atm. absolute. By preparing a plot of absolute pressure against saturated liquid volume (*25*, 3rd ed., p. 274), the proper value of v is obtained as 1.316 cu. ft. per lb. mole, so that

$$\alpha = (83.5/1.316)(10^{-11}) = \frac{(63.5)(10^{-11}) \text{ lb. mole adsorbed}}{\text{sq. ft. of surface area}}$$

Differential isosteric heats of adsorption were calculated for the hydrocarbons. The heat values, Q_a, as a function of fraction

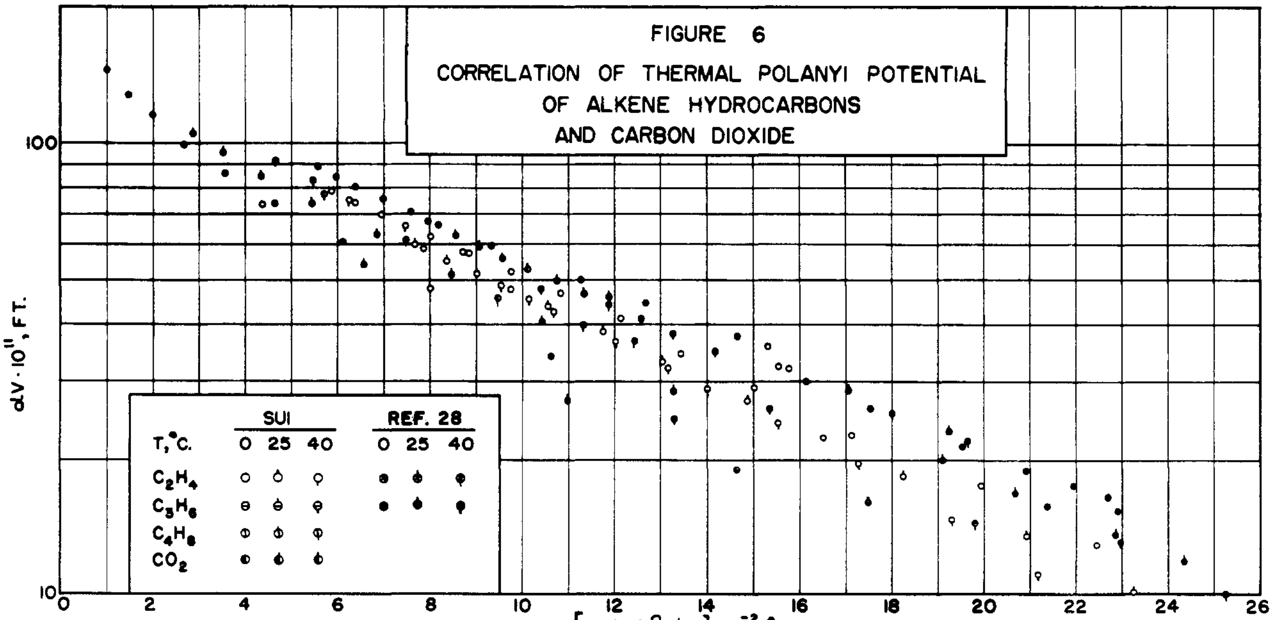
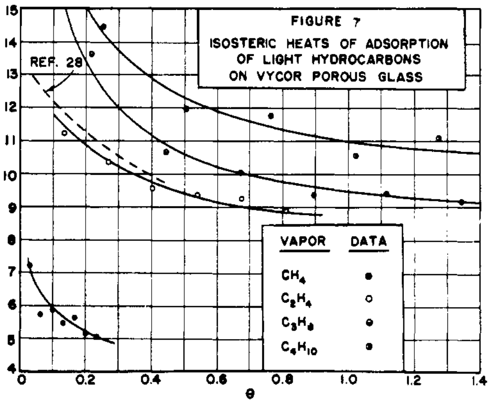


FIGURE 6
CORRELATION OF THERMAL POLANYI POTENTIAL OF ALKENE HYDROCARBONS AND CARBON DIOXIDE

of monolayer capacity θ were calculated from the slopes of the log P *vs.* $1/T$ plot of the adsorption isosteres. Noting that $Q_a/R = (\partial \ln P)/\partial(1/T)$, values of Q_a can be calculated by graphically measuring the slope from the plot at various points.

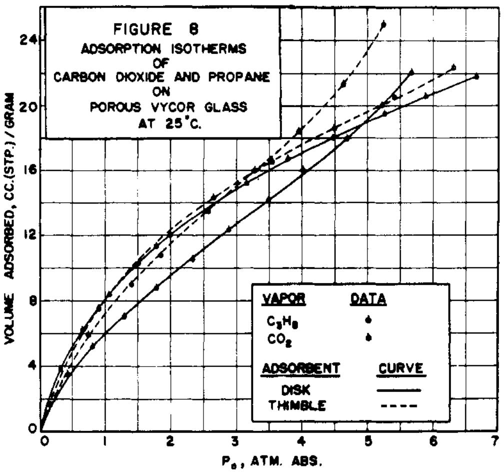
The data for the alkanes and for ethene are presented in Figure 7. The corresponding values of propene and 1-butene would fall below the ethene data, which is contrary to what one would expect from a mechanism of physical adsorption. Russell's (*28*) data for ethene are also shown on Figure 7; his data for propene would be about 12% above the ethene data, while the author's propene values would be about 12% below. 1-Butene values of this work would lie below his propene data. Because of the uncertainty created by this situation, neither the Russell data nor the author's are shown on Figure 7.

Carbon Dioxide and Propane. Adsorption data for carbon dioxide and propane have an interesting relation to the barrier separation experiments (*10*). The separation data showed that propane became enriched in passing through a porous glass barrier, and this behavior was ascribed to a greater degree of propane adsorption compared to carbon dioxide adsorption.



While the occurrence of selective adsorption can readily be used to explain the separation data, it was hoped that the adsorption isotherm of the individual components would show that propane adsorption was greater than carbon dioxide adsorption. If this had been the case, the situation would have been fairly simple.

What actually happened is shown in Figure 8, where adsorption isotherms at 25° C. for the two vapors are presented for both the porous glass disks and the thimble-shaped structure. The curves do not represent adsorption from mixtures. The separation data obtained with the thimble at 25° C. (*10*) gave enrichment of propane over the pressure range of 1.33 to 2.33 atm. absolute. In this pressure range, the carbon dioxide adsorption (pure component adsorption) was the greater one at 25° and 40° C., and became equal to the propane adsorption at about 2.4 atm. absolute and 0° C. Consequently, it is still necessary to assume preferential adsorption of propane from the vapor mixtures, which varied in composition from 25 to 74% carbon dioxide. At present, no data are available on the adsorption behavior of such mixtures. The behavior of many hydrocarbon systems with silica gel and activated carbon has been described by Lewis and others (*11*), and mutual interference of adsorption was found with the mixtures in all cases. Selective adsorption behavior of vapor mixtures of methanol and benzene was studied by Reeds (*27*). In that work, the existence of an adsorption azeotrope was established, so that preferential adsorption of either component would occur, depending on the composition of the vapor mixture. Therefore, the assumption of preferential propane adsorption from the propane–carbon dioxide mixtures should constitute a reasonably valid interpretation.



ACKNOWLEDGMENT

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