Adsorption from Vapor Mixtures

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ADEQUATE EXPERIMENTAL evidence exists to show that adsorption influences the diffusion of gases through microporous barriers (*4, 8, 9*). Kammermeyer and Wyrick (*8*) studied the permeation-separation characteristics of carbon dioxide–propane mixtures through porous 96% silica glass, and observed that the permeated gas became enriched in propane. The enrichment cannot be explained by free-molecule diffusion alone because a mixture of compounds of essentially equal molecular weight should not undergo any separation. They deduced that the enrichment of propane may be entirely due to the separation mechanism of adsorbed phase flow. Since no data were available for the adsorption of carbon dioxide–propane mixtures on porous 96% silica glass, this could not be confirmed at that time.

This investigation determined the amounts of adsorbed carbon dioxide and propane in equilibrium with their respective gas phases. Measurements were made at various pressures, temperatures, and gas compositions to study the effect of these variables on the degree of adsorption of each component. Adsorption was studied at three temperatures: 0°, 30°, and 50° C. The pressures investigated ranged from 1 to 4 atm. absolute for the gas mixtures, and from 0.5 to 7.3 atm. absolute for the pure gases.

EXPERIMENTAL

Apparatus. The adsorption apparatus has been described by Rutz, Graham, and Kammermeyer (*16*). A pump was incorporated into the apparatus to circulate the gas. The gas circulating pump was a model LS-10 Microflo Pulsafeeder diaphragm pump, manufactured by the Lapp Insulator Co. The diaphragm was made of Kel-F plastic. For a negligible difference between intake and discharge pressures, the pump delivered 2100 cc. of air per hour at 25° C. and 755 mm. of Hg. The pressure drop around the gas circulation path in the apparatus was negligible. Gas pressures in the apparatus were measured with the mercury manometer (*16*).

Gas mixture analyses were made with a simplified Orsat gas analyzer which consisted of a water-jacketed, 100-ml. gas measuring buret, leveling bulb, and a gas adsorption pipet containing a 30% (by weight) KOH solution. The leveling bulb contained mercury.

Adsorbent. Five porous 96% silica glass disks were used as the adsorbent sample. This glass is an intermediate product in the manufacture of Corning glass. The void fraction, specific surface area, and average pore diameter were determined from gas displacement or adsorption measurements. The void fraction of these adsorbent samples was 0.33. The specific surface area of similar porous glass samples was determined to be about 200 sq. meters per gram (*14*). The average pore diameter is about 50 A. (*11*).

The glass samples were cleaned by boiling in concentrated nitric acid, then boiled in several portions of distilled water, and heated slowly to 450° C.

Adsorbates. The adsorbates used were "bone dry grade" carbon dioxide and "instrument grade" propane, both obtained from the Matheson Co. The purities of the carbon dioxide and propane were 99.8 and 99.9%, respectively.

Procedure. The method for determining the pure gas isotherms was similar to the one previously developed (*16*). For the gas mixture determinations, propane and carbon dioxide were premixed in auxiliary tanks. Before each adsorption determination, the apparatus was evacuated for at least 12 hours. A portion of the gas mixture was let into the high pressure side of the apparatus, and then analyzed. After the pressure and temperature were recorded, the gas was allowed to expand into the vessel containing the adsorbent sample, and the diaphragm pump was started. The gas mixture was circulated through the system for 6 to 8 hours. After the pump was turned off, the pressure was measured. Finally, the sample side of the apparatus was shut off from the high pressure side for analysis. The amount of each component adsorbed was calculated from the change in gas composition and pressure.

RESULTS

Pure Gases. The data plotted in Figure 1 show that pure carbon dioxide was more strongly adsorbed than pure propane at the same temperature and pressure over the whole pressure range investigated for the 30° and 50° C. isotherms; at 0° C., carbon dioxide was more strongly adsorbed up to 2.37 atm. absolute. Above 2.37 atm. absolute, propane was adsorbed to a greater degree. The amounts adsorbed for both pure gases were slightly less than the values reported by Rutz, Graham, and Kammermeyer (*16*) for porous glass disks. The ratio of values to their's at corresponding conditions is 0.928. The ratio of Brunauer-Emmett-Teller areas for carbon dioxide at 0° C. is also 0.928. Rutz, Graham, and Kammermeyer also reported differences in adsorption for different porous glass samples. They found that carbon dioxide and propane adsorbed more strongly on porous glass thimbles than on porous glass disks. It seems likely that the variation in adsorption was primarily due to differences in the specific surface areas. Variations in pore size may also contribute to variations in adsorption.

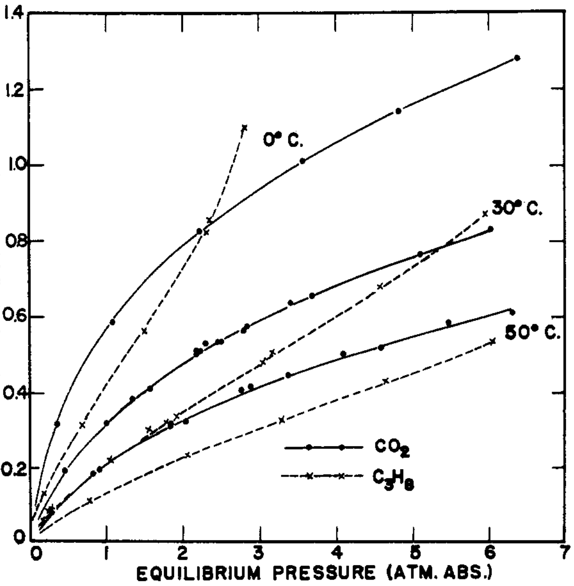

Figure 1. Adsorption of pure carbon dioxide and pure propane on porous glass

Figure 2 shows a thermal Polanyi potential correlation for pure carbon dioxide and for pure propane. Lewis and others (*9*) expressed the adsorption potential as [$RT \ln(f_s/f)$].

The volume of the adsorbed phase is (NV), where N is the number of moles of gas adsorbed and V is the molal volume of the gas in the adsorbed phase. Since little is known about adsorbed phase densities, assumed molal volumes must be used. The molal volume of the adsorbed phase at a given equilibrium pressure is assumed equal to the molal volume of the saturated liquid at that same pressure (*9*). Molal volumes of propane and carbon dioxide were calculated from data given by Perry (*3*). For carbon dioxide, saturated liquid volumes were extrapolated below the triple point by the generalized data of Lydersen, Greenkorn, and Hougen (*10*).

Vapor pressure data were taken from Perry (*3*). An extrapolated value of 114 atm. absolute was used for the vapor pressure of carbon dioxide at 50° C. Fugacities for both propane and carbon dioxide were calculated from Maxwell's generalized charts (*12*).

The group, [$T \ln(f_s/f)$], called the thermal Polanyi potential after Rutz and others (*16*) is obviously proportional to [$RT \ln(f_s/f)$]. For the same adsorbate and adsorbent, Figure 2 shows that, within the limits of experimental accuracy, [$T \ln(f_s/f)$] depends only upon (NV) in agreement with the Polanyi theory. Therefore other isotherms can be predicted with considerable accuracy.

Gas Mixtures. Within the ranges of temperature, pressure, and composition covered in this investigation, carbon dioxide was always preferentially adsorbed from the gas mixtures.

The relation between phase compositions can be expressed as a relative volatility (α) of propane with respect to carbon dioxide where

$$\alpha = \left(\frac{y}{1\text{-}y}\right)\left(\frac{1\text{-}x}{x}\right) \tag{1}$$

where

y = mole fraction propane in gas phase
$1\text{-}y$ = mole fraction carbon dioxide in gas phase
x = mole fraction propane in adsorbed phase
$1\text{-}x$ = mole fraction carbon dioxide in adsorbed phase

The effect of pressure upon the relative volatility at 30° C. is shown by Figure 3. At all temperatures the relative volatility decreased with increasing pressure, in accord with the findings of Lewis and others for alkane-alkene mixtures on charcoal and silica gel (*9*).

The type of plot used to present the experimental data was determined by the nature of the apparatus. Since the gas volume remained constant and, therefore, the pressure of the gas adjusted to attain equilibrium, it would have been exceedingly difficult to attain a fixed equilibrium pressure and so obtain constant pressure data. However, the adsorbed phase composition for a given initial gas sample varied little with pressure. The constant composition lines of Figure 3 were then drawn through points representing equilibrium where the adsorbed phase compositions were nearly equal. The composition was taken to be the arithmetic mean of the individual adsorbed phase compositions. Subsequent readjustment, from cross plots, of the constant composition lines due to the actual variation in adsorbed phase composition proved to be negligible compared to experimental error.

All information concerning equilibrium behavior at constant pressure had to be obtained from cross plots. At all temperatures the relative volatility increased with increasing propane concentration. The equilibrium compositions of the gas and adsorbed phases at constant temperature and pressure were calculated from cross plots. The results of these calculations for 30° C. are shown in Figure 4.

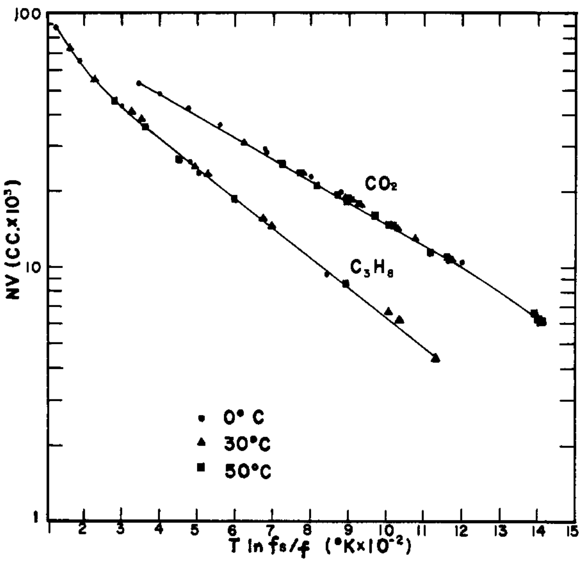

Figure 2. Thermal Polanyi potential correlation for pure carbon dioxide and pure propane on porous glass

Adsorbed Phase Correlation. Lewis and others (*9*) suggested and empirical correlation of the number of moles of each component adsorbed from a gas mixture with the number of moles of each component adsorbed from its pure gas at the same temperature and total pressure.

The correlation is expressed by the equation

$$\frac{N_1}{N_1'} + \frac{N_2}{N_2'} = 1 \tag{2}$$

where

N_1 = moles of Component 1 adsorbed from the mixture
N_1' = moles of Component 1 adsorbed from its pure gas at the temperature and total pressure of the mixture
N_2 = moles of Component 2 adsorbed from the mixture
N_2' = moles of Component 2 adsorbed from its pure gas at the temperature and total pressure of the mixture

Lewis (*9*) found that this correlation held within 6% for all the systems he investigated except methane-ethylene mixtures on silica gel.

The adsorbed phase correlation for propane–carbon dioxide mixtures on porous glass is shown in Figure 5. The diagonal line represents Equation 2. Nearly all data points are above this line. The relative standard deviation of the data from the dashed curve is about 7%. The greatest amount of scatter is found in the data for 0° C. Obviously, the CO_2–C_3H_8 adsorption behavior on porous 96% silica glass cannot be expressed to a satisfactory degree by means of the Lewis correlation.

SIGNIFICANCE OF DATA

The prediction of adsorption is a necessary part of the design of adsorptive-separation processes. At present pure gas adsorption can be predicted with considerable accuracy by Polanyi correlations (*15*), and by adsorption equations such as the Brunauer-Deming-Deming-Teller equation.

The correlation of gas mixture adsorption data is more difficult. The adsorbed phase correlation for carbon dioxide–propane mixtures shown in Figure 5 does not conform to the linear displacement model postulated by Lewis and others (*9*). The difficulty probably lies in evaluating the interaction between the different components in the adsorbed phase.

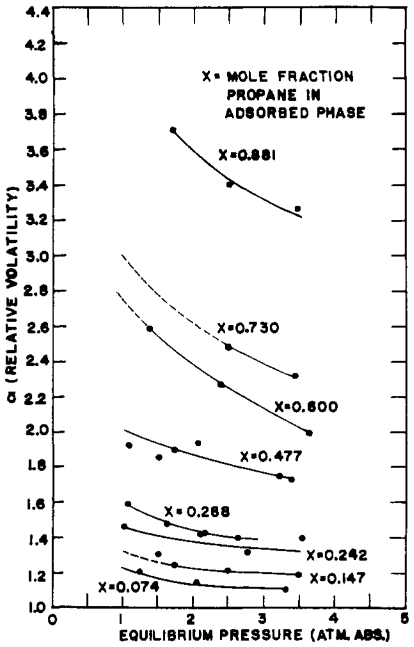

Figure 3. Effect of pressure on relative volatility at 30° C.

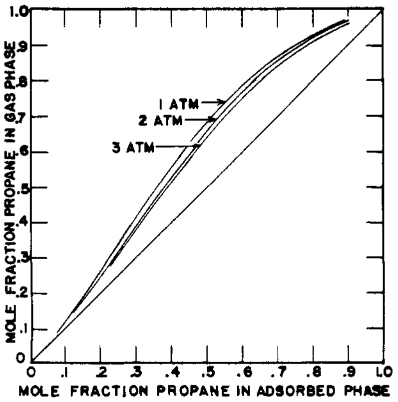

Figure 4. Equilibrium composition plot for 30° C.

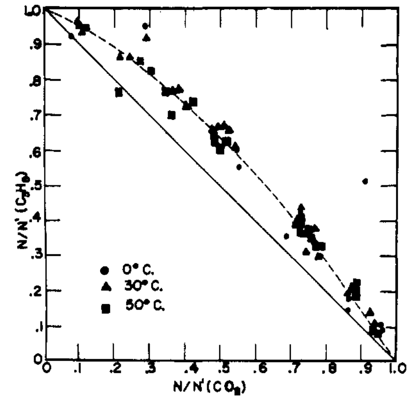

Figure 5. Adsorbed phase correlation

It was hoped that data on the adsorption of a gas mixture would help explain the mechanism of adsorbed or surface flow. There can be little doubt that surface flow does occur and that it is tied up with adsorptive behavior.

Data from studies of the mechanism of Knudsen diffusion of pure gases through porous 96% silica glass (*6*, *17*) have shown greater flows than postulated by the Knudsen mechanism. Furthermore, a number instances of well documented data show separations in gas or vapor mixtures (*1*, *5*, 6), that leave no doubt that adsorption behavior has a major effect on these separations.

For carbon dioxide-propane mixtures in particular, the separation data of Kammermeyer and Wyrick (*8*) for the equimolecular weight pair displays an enrichment of propane in the permeated gas stream. On the other hand, adsorption data show that carbon dioxide is more strongly adsorbed from mixtures than propane.

These two phenomena can be reconciled best by the model of activated surface diffusion outlined by Carman (*2*). According to this model the amount of surface flow is:

$$n = -D_s \nabla c \qquad (3)$$

where

n = amount of a component flowing through the barrier by surface diffusion, moles/sq. cm. -sec.
D_s = surface diffusion coefficient for the component, sq. cm./sec.
∇_c = concentration gradient of the component in the adsorbed phase, moles/(cc. of barrier) (cm. thickness)

Also, according to this model, the surface diffusivity depends upon temperature and an activation energy:

$$D_s = K \exp.(-E_a/RT) \qquad (4)$$

where

K = proportionality constant
E_a = energy required for a molecule to move from one adsorption site to another
R = universal gas constant
T = absolute temperature

Therefore, the amount of a component transported by surface flow will be greater for larger values of the pre-exponential term, K, for larger concentration gradients and for smaller activation energies. The following approximate values for K and E_a were calculated from the pure component permeability data (*8*):

	C_3H_8	CO_2
K, sq. cm./sec.	0.005	0.0002
E_a (cal./g. mole	2000	9000
Av. amount adsorbed, cc.stp./g. adsorbent	8.5	12.5

According to Carman (*2*) the pre-exponential term, K, is roughly proportional to the average distance between adsorption sites, while the activation energy is a measure of the bonding strength of the adsorbate to the solid surface.

Michaels and Barrie (*13*) have suggested, that carbon dioxide, being more polar than propane, may be strongly bonded to specific localized sites on the solid surface, which would account for the low surface mobility of carbon dioxide, in spite of its high surface concentration. The above values for K and E_a from Carman's model support this explanation.

It is usually assumed (*2*) that gas phase concentration gradients in a porous matrix are linear and that the adsorbed phase is in equilibrium with the gas phase at every point. In order to calculate adsorbed phase diffusivities from gas mixture permeabilities or vice-versa according to this model, adsorption equilibrium data are required.

For this system, we have shown by Figure 5 that gas mixture adsorption cannot be correlated well with pure component adsorption by the Lewis method. Neither can gas mixture adsorption be predicted accurately by assuming that the amount of each component adsorbed from a mixture is the same as the amount of the components adsorbed from their pure gases at pressures equal to their partial pressure in the mixture. We suggest that there may be appreciable competition for adsorption sites, even though carbon dioxide seems to be strongly bonded to specific sites.

It also seems likely that interaction between components in the adsorbed phase would affect the adsorbed phase diffusivities. Since we cannot confidently extrapolate nor interpolate the gas-mixture data of this study to the temperature of Kammermeyer and Wyrick's investigation, it is not possible to calculate adsorbed phase diffusivities from their separation data.

Michaels and Barrie (*13*) have further suggested that a third transport mechanism ought to be considered as follows:

> Since the critical temperature of propane is higher than that of carbon dioxide, it seems possible that, at the pressures and temperatures involved, propane might actually undergo capillary condensation in the smaller pores of the plug. If this were to occur, rather rapid transport

could take place through these liquid filled capillaries, yielding an over-all flux of propane far in excess of that which might be anticipated on a basis of its average concentration in the plug as a whole. Furthermore, capillaries filled with liquid propane would not be readily accessible to carbon dioxide, so that the transport rate of carbon dioxide would be correspondingly reduced.

Data of Kammermeyer and Wyrick showed that the apparent surface diffusivities for propane increased rapidly with average pressure at −5° and 12° C., which could be explained by capillary transport. However, even such a seemingly plausible explanation must be treated with caution, as permeability data for ammonia on porous glass (*7*) showed that the permeabilities decreased from peak values when condensation conditions were approached.

LITERATURE CITED

(1) Brubaker, D.W., Kammermeyer, K., "Separations in the Gaseous Phase by Means of Porous Membranes," Proc. 1953 Conf. on Nuclear Eng., Univ. of Calif., Berkeley, F-27.
(2) Carman, P.C., "Flow of Gases through Porous Media," pp. 108–22, Academic Press, New York, 1956.
(3) "Chemical Engineers' Handbook," J.H. Perry, ed., 3rd ed., pp. 149, 163, 254, 274, McGraw-Hill, New York, 1950.
(4) Gilliland, E.R., Baddour, R.F., Russell, J.L., *A.I.Ch.E. Journal* **4**, 90 (1958).
(5) Hagerbaumer, D.H., Kammermeyer, K., *Chem. Eng. Progr. Symp. Ser. No. 10,* Collected Research Papers for 1954, **50**, 25–44 (1954).
(6) Huckins, H.E., Kammermeyer, K., *Chem. Eng. Progr.* **49**, 180, 294 (1953).
(7) Kammermeyer, K., *Chem. Eng. Progr. Symp. Ser.* No. 24, **55**, 115–25 (1959).
(8) Kammermeyer, K., Wyrick, D.D., *Ind. Eng. Chem.* **50**, 1309 (1958).
(9) Lewis, W.K., Gilliland, E.R., Chertow, B., Cadogan, W.P., *Ibid.*, **42**, 1326 (1950).
(10) Lydersen, A.L., Greenkorn, R.A., Hougen, O.A., "Report 4, Generalized Thermodynamic Properties of Pure Fluids," Engineering Experiment Station, Univ. of Wisconsin, Madison, Wis., 1955.
(11) Lyon, L.L., Crocker, G.R., Heldman, M.J., Fisher, J., "Surface Areas of Finely Divided Materials," Rept. COO-142, Univ. of Wichita Foundation for Industrial Research, Wichita, Kan., 1953.
(12) Maxwell, J.B., "Data Book on Hydrocarbons," p. 62, Van Nostrand, New York, 1950.
(13) Michaels, A.S., Barrie, J.A., Mass Inst. Technol., Cambridge, Mass., unpublished communication, Sept. 12, 1961.
(14) Nordberg, M.E., *J. Am. Chem. Soc.* **27**, No. 10, 299 (1944).
(15) Polanyi, M., *Verhandl. deut. physik. Ges.* **16**, 1012 (1914).
(16) Rutz, L.O., Graham, J.B., Kammermeyer, K., J. CHEM. ENG. DATA **4**, 307 (1959).
(17) Rutz, L.O., Kammermeyer, K., U. S. At. Energy Comm. (Unclassified) Rept. **3921**, Office of Tech. Services, Dept. of Commerce, Washington 25, D. C., 1958.

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Extraction of Benzene with Di- and Triethylene Glycols

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THE UDEX SYSTEM (*2, 3*) for recovery of aromatics from mixtures of aromatics and saturates by solvent extraction normally requires a mixture of diethylene glycol and water as the solvent. The extraction column and stripper for recovery of solvent from the extract stream are usually operated between 250° and 300° F. The only equilibrium data available for this aqueous system were taken at temperatures of 257° F. and below (*1*). The present work presents equilibrium data at 250° and 300° F. for both diethylene and triethylene glycol with two different water concentrations.

MATERIALS

The equilibrium curves were determined from tie line data and cloud point measurements. In each case the phases were contacted in a high pressure bomb previously designed and built for this purpose. The bombs were built of stainless steel with sight glasses fitted on opposite sides so that it was possible to observe the contents at all times. A stirrer was built into the bomb and was actuated with a solenoid coil. The bomb was equipped with three 0.125-inch stainless steel sampling or charging tubes. One went to the bottom, one went to approximately the middle, and one went to the top of the mixing chamber.

The desired temperatures were obtained by immersion in a constant temperature oil bath of Dow Corning 550 fluid. A thermowell was built into the bomb to facilitate temperature measurement of the fluids being contacted. The temperature was determined with a portable precision potentiometer, using an iron-constantan thermocouple.

EXPERIMENTAL PROCEDURES

The components were all charged to the bomb through the tube that went to the bottom of the chamber. The bomb was washed with distilled water and then acetone, dried with air, and then evacuated. The glycol phase was charged first, the saturate phase second, and the benzene last, in an effort to minimize any liquid holdup on the tube walls. In every case a sample bottle was tared, the liquid was introduced into the bottle, and it was weighed again. The