Adsorption of Propane and Propylene on Silica Gel at Low Temperatures

FRANK MASLAN[1]
Department of Chemical Engineering, The University of Connecticut, Storrs, CT 06268

ETIENNE R. ABERTH
Department of Chemical Engineering, New York University, University Heights, New York, NY 10453

Adsorption isotherms for pure propane and propylene on silica gel were determined at 0°, −20°, and −35°C from 5–760 mm Hg pressure. A McBain balance apparatus with a regulated refrigerant thermostat was used. These experimental data were correlated within 3% deviation by the Polanyi-Dubinin-Lewis potential theory in which the adsorbate liquid volume is calculated at the experimental temperature.

Adsorption is being used increasingly as a separation process for hydrocarbon mixtures. Lewis et al. determined isotherms for propane and propylene on silica gel at 25°C (*2*). For the purposes of this work more data over a range of lower temperatures were required. Therefore isotherms for propane and propylene on silica gel were determined at 0°, −20°, and −35°C over the range of 5–760 mm Hg pressure.

Lewis et al. (*1*) have derived a successful correlation method based on the Polanyi-Dubinin potential theory. In their correlation, log NV' ordinate is plotted against T/V' log (f_s/f) abscissa. For V' they used the molal volume of the saturated liquid adsorbate at a temperature at which the vapor pressure is equal to the adsorption pressure. Since our work was carried out below the critical temperatures of propane and propylene, it was decided to test a modified correlation. As in Dubinin's original correlation (*3*), the molal volume of the adsorbate, V, was taken as a saturated liquid at the experimental adsorption temperature. The basic reason for this is that the temperature of the adsorbate is known experimentally and is fixed, while any uncertainty is concerned with the adsorption vapor pressure assumed in the Lewis correlation. Except for the molal volume modification, this method is the same as the Lewis correlation.

EXPERIMENTAL

The adsorption isotherms were determined on a McBain balance apparatus. The glass tube holding the McBain balance was designed with a thin wrapping of nichrome electric heating ribbon inside a surrounding vacuum jacket, 0.5 in. wide. A refrigerant bath of acetone and Dry Ice in a separate Dewar vacuum flask surrounded this apparatus on the outside of the thin vacuum jacket up to several inches above the bucket. Thus the vacuum jacket, in which the vacuum could be adjusted, acts as an insulator between the acetone–Dry Ice bath and the adsorption tube; and heat can be applied by the resistance nichrome ribbon wound around the outside wall of the adsorption tube. This experimental method allowed the maintenance of stable temperatures. A shielded copper-constantan thermocouple calibrated at low temperature by standard methods was placed adjacent to the bucket holding the silica gel sample. This gave the same temperature readings as when placed inside the empty adsorbent bucket. A beryllium-copper spring was used for suspending the bucket, and the elongation was measured with a cathetometer. This spring elongated linearly at 0.3910 g/cm over the experimental range. The possible errors in precision of the measured quantities were as follows: pressure, less than 0.1 mm Hg; temperature less than 0.1°C; and weight adsorbed less than 0.0005 gram.

The temperature of the acetone bath was approximately 10°C lower than the experimental adsorption temperature desired. This was controlled by adding Dry Ice to the acetone. The lowest adsorption isotherm was determined at −35°C because the boiling points of propane and propylene are −42.2° and −47.7°C, respectively, and condensation of the gases could occur in the experimental apparatus if temperatures lower than −35°C were attempted.

The adsorbent used was silica gel, Davison PA-100, refrigeration grade, BET surface area of 751 m^2/g using the nitrogen isotherm. This was obtained from Davison Chemical Co. Division, W. R. Grace Corp. The propane was more than 99.7% pure. The principal impurities were approximately 0.2% ethane and butane. The propylene was more than 99.7% pure and the principal impurity was propane. Both the propane and propylene were obtained from the Matheson Co., Inc., East Rutherford, NJ.

The weight of the adsorbent silica gel was obtained by putting a measured amount of previously dried regenerated silica gel in the bucket and then evacuating to a pressure of 0.1 μ for 2 hr at a temperature of 170°C. The silica gel lost a very small amount of weight during this 2-hr evacuation period. This loss in weight of the sample was observed by measuring the spring elongation with the cathetometer. The weight of the silica gel after the 2-hr evacuation and heating period was taken as the initial weight of the experimental adsorbent sample. After each cycle of adsorption and desorption, the silica gel sample was regenerated by evacuation at a pressure of 0.1 μ or less and a temperature of 170°C for 1 hr. The sample was then allowed to cool to room temperature while kept under the high vacuum. This reactivation method gave good reproducible results.

DISCUSSION

The experimental results are given in Table I. These data give good smooth isotherm curves for both propane and propylene. The isotherms are flatter than propane and propylene isotherms on activated carbon, but are similar to the one for silica gel at 25°C presented by Lewis et al. (*2*).

As would be expected, the low-temperature isotherms determined here show a much higher adsorption capacity than the

[1] To whom correspondence should be addressed.

Table I. Adsorption Isotherms of Propane and Propylene on Silica Gel

Temp, °C	Press., mm Hg	G adsorbed/g silica gel
	Propane	
−35	15	0.035
	59	0.069
	162	0.109
	300	0.157
	470	0.194
	576	0.209
	640	0.214
	662	0.216
	732	0.216
−20	17	0.021
	66	0.048
	109	0.068
	208	0.093
	312	0.114
	459	0.138
	616	0.161
	762	0.180
0	25	0.014
	71	0.027
	129	0.040
	216	0.055
	322	0.069
	467	0.087
	616	0.102
	754	0.115
	Propylene	
−35	6	0.042
	37	0.091
	96	0.124
	179	0.156
	306	0.179
	455	0.204
	609	0.222
	746	0.233
−20	5	0.027
	45	0.068
	109	0.094
	209	0.117
	319	0.137
	468	0.154
	620	0.171
	745	0.187
0	16	0.025
	67	0.048
	111	0.062
	211	0.081
	312	0.096
	469	0.112
	621	0.125
	760	0.134

Lewis 25°C curve. The isotherm data on silica gel indicate a definite preferential adsorption of propylene. Again this agrees with the Lewis work in which they reported unsaturated paraffinic hydrocarbons are adsorbed to a greater extent on silica gel than are saturated ones.

These isotherms give enough data so that the effect of temperature on the adsorption capacity of silica gel can be examined by the Polanyi theory. The data from Table I were correlated first by the method presented by Lewis et al. (*1*) with an average deviation of 3%. Separate curves for propane and propylene were obtained which is in agreement with the Lewis results.

Then the previously discussed modification was used in calculating the molal liquid volume, giving the curves presented in Figure 1. In this figure the molal liquid volume was calculated at the experimental temperature. Good correlation was obtained with an average deviation of less than 3%. This temperature choice is the one originally proposed by Dubinin (*3*), but not tested before for propane and propylene. It is clear that it applies very well below the critical temperature of these adsorbates.

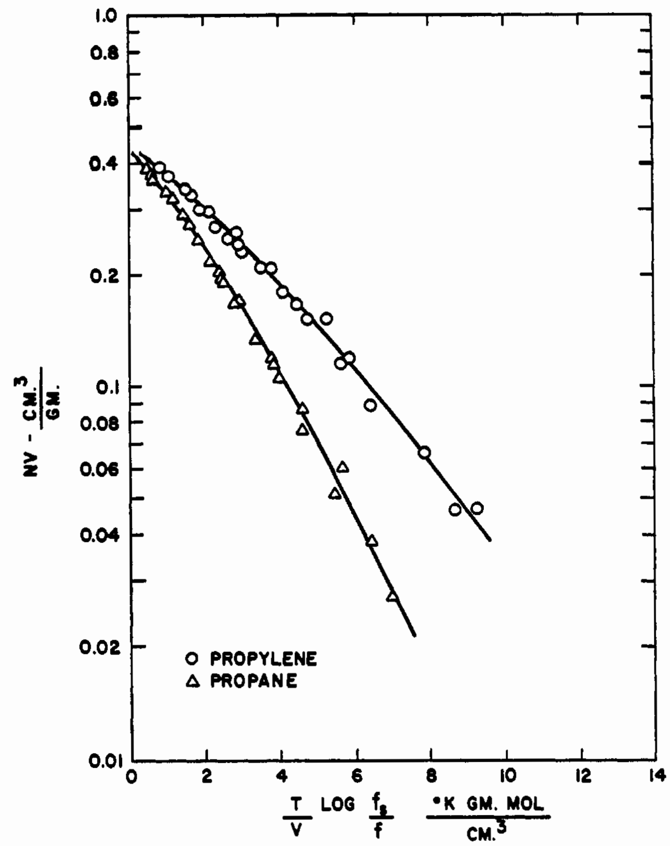

Figure 1. Polanyi potential theory correlation of isotherms for propane and propylene on silica gel

Both of these correlation methods give good accuracy, and a choice depends on convenience of application. These correlations, combined with the data presented, can be used to cover a wide range of temperature and pressure.

NOMENCLATURE

N = amount adsorbate adsorbed, moles per unit weight of adsorbent
T = temp, K
V = molal volume of saturated liquid adsorbate at adsorption temp, cc/g mol
V' = molal volume of saturated liquid adsorbate at a vapor pressure equal to adsorption pressure, cc/g mol
f = fugacity at adsorption pressure, atm
f_s = fugacity of saturated liquid adsorbate at adsorption temp, atm

LITERATURE CITED

(1) Lewis, W. K., Gilliland, E. R., Chertow, B., Cadogan, W. P., *Ind. Eng. Chem.*, **42**, 1326 (1950).
(2) Lewis, W. K., Gilliland, E. R., Chertow, B., Hoffman, W. H., *J. Amer. Chem. Soc.*, **72**, 1153 (1950).
(3) Young, D. M., Crowell, A. D., "Physical Adsorption of Gases," p 141, Butterworths, Washington, DC, 1962.

Received for review September 20, 1971. Accepted February 28, 1972.