EQUILIBRIUM ADSORPTION OF METHANE AND CARBON DIOXIDE ON 5A MOLECULAR SIEVE

Dr. Abbas Khalaf Mohammed Shua'ab
Chemical Engineering Department, Baghdad University, P. O. Box 47024, Baghdad, Iraq

ABSTRACT

Experimental and theoretical studies have been carried out to study the adsorption of methane and carbon dioxide on 5A molecular sieve. Adsorption equilibrium isotherms of methane and carbon dioxide are reported for the temperature range 303–333 K and pressure up to 2.5MPa. Experimental data were obtained using a static system for gas–solid adsorption. The Langmuir adsorption equilibrium equation gave good predictions. Adsorption of methane and carbon dioxide on 5A molecular sieve is purely physical since the isosteric heat of adsorption was found to be equal to 14.804 and 37.218 kJ mole^{-1} for methane and carbon dioxide, respectively.

الخلاصة

تم الحصول على توازن الامتزاز الايزوثرمي لغاز الميثان و غاز ثاني اوكسيد الكربون باستخدام المناخل ألجزيئيه نوع 5A و عند درجات حرارة تتراوح من ٣٠٣كلفن إلى ٣٣٣كلفن و ضغط يصل إلى ٢,٥ميكاباسكال. النتائج ألمختبريه تتطابق بشكل جيد مع النموذج التجريبي للانكماير. امتزاز غاز الميثان و غاز ثاني اوكسيد الكربون على المناخل ألجزيئيه نوع 5A هو امتزاز فيزياوي وذلك بسبب إن حرارة الامتزاز لغاز الميثان تساوي ١٤,٨٠٤كيلوجول/مول و لغاز ثاني اوكسيد الكربون تساوي ٣٧,٢١٨كيلوجول/مول.

KEYWORDS
molecular sieve; adsorption; methane; carbon dioxide)

INTRODUCTION

The increasing importance of adsorption processes for the separation of gaseous mixtures is due to the high selectivity and adsorption capacity of solid adsorbents, the less extreme operation conditions needed, and the small energy consumption required. Adsorption is becoming a competitive operation that can advantageously substitute for other separation operations such as distillation or absorption. The advantages are especially attractive when the problem is the separation of light gases, since their separation by distillation or absorption requires expensive high pressure units.

The adsorptive separation is achieved by one of the three mechanisms: steric, kinetic or equilibrium effect. The steric effect derives from the molecular sieving property of zeolites. In this case only small and properly shaped molecules can diffuse into the adsorbent, whereas other molecules are totally excluded. Kinetic separation is achieved by virtue of the difference in diffusion rates of different molecules into the adsorbent. By far, however, most processes operate through the equilibrium (or competitive) adsorption of the mixture, and hence are called equilibrium separation processes. Commercial separation processes using molecular sieve zeolites are mainly equilibrium processes (Kapoor & Yang, 1989).

Separation of bulk gas mixtures containing methane and carbon dioxide is an important problem in the chemical industry. Many natural gas reservoirs contain up to 50% CO_2 as impurity. The effluent gas from an oil well undergoing CO_2 flooding for enhanced oil recovery may contain 20–80% CO_2 and CH_4. It may be necessary to separate the CH_4 and the CO_2 from these gases in order to improve their fuel value and to recover and reuse the CO_2.

Data on the adsorption of methane and carbon dioxide on molecular sieves are scarce in the literature. Some low–pressure data and correlations have been reported for Linde 5A and 13X molecular sieve, where carbon dioxide was found to be preferentially adsorbed on the former molecular sieve (Tańczyk & Warmuziński, 1998; Kumar, 1989; Hyun & Danner, 1982). Limitation are placed on the usefulness of these data for the design of commercial molecular sieve–based separation systems, since a large part of these data was obtained at temperatures and pressures which are not ordinarily considered practical from a commercial stand point.

This paper reports a fundamental equilibrium adsorption data obtained for methane and carbon dioxide on a single sample of 5A molecular sieve (supplied by Rhone Poulenc industries). To simulate industrial conditions, the temperature ranged from ambient to 60 ˚C and the pressure to 2.5 MPa. These data are of value in process and design studies of 5A molecular sieve–based separation systems involving the separation of carbon dioxide from natural gas and oil well effluent.

EXPERIMENTAL WORK

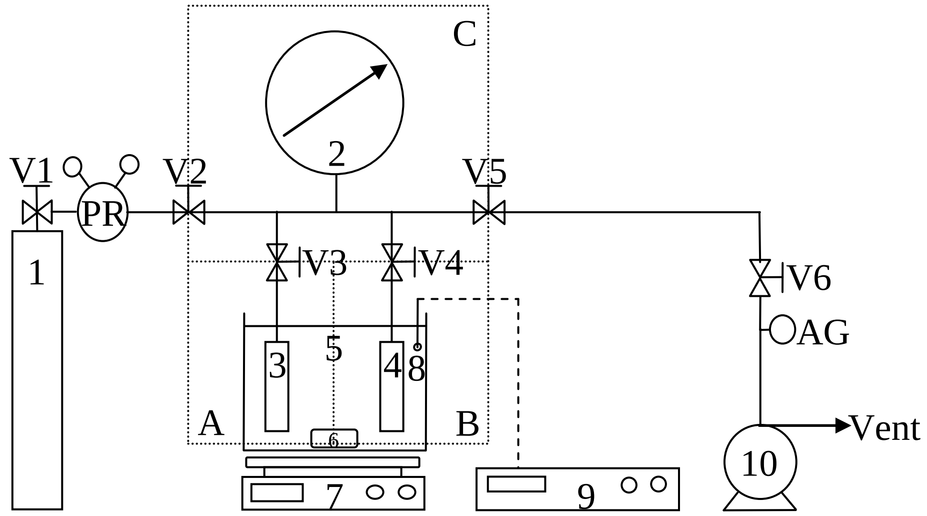
A schematic diagram of the apparatus is shown in figure 1. All tubing was thick wall stainless steel, to minimize the dead volume. The tubing was connected by Crawford Swagelock compression fittings. Parker CPI series severe service union bonnet valves, with a hardened ball stem tip, were chosen because of their durability under repetitive use. A metal stem tip was selected instead of a soft stem tip to avert destruction of the valve seat in the event that particulate matter should escape from the adsorption chamber, enter the valve and score the valve seat.

The adsorption chamber and reservoir were 20 cm^3 iron sample cylinders. Entrainment of adsorbent particles in the tubing and valving system was prevented by employing a dual screen method. This was accomplished by inserting Pyrex glass wool and a conical brass wire mesh screen, capable of containing particles.

The gas pressure was measured via a Heise bourdon gauge with a 430 mm diameter dial and a pressure range from 0 to 6891 kPa. The accuracy of the gauge was rated at 0.1% of the full scale and the sensitivity at 0.02% of the full scale at all points. The pressure gauge enclosed a dead volume of approximately 30 cm^3.

A water bath was employed to provide a constant temperature environment up to 353 K for both the adsorber and the reservoir. The bath was thermo–stated and vigorously mixed by using a magnetic stirrer thermo–stat hot plate. The temperature of the bath was continuously measured and recorded via a digital recorder and a thermocouple wire, calibrated with mercury thermometer.

The whole equipment was evacuated by vacuum pump and absolute gauge pressure prior to each experiment. The feed gas supplied from cylinder was regulated by pressure regulator.\



1	Gas cylinder	6	Stir bar	V	Manual valve
2	Heise pressure gauge	7	Magnetic stirrer thermostat hot plat	PR	Pressure regulator
3	Reservoir bomb	8	Chromel–alumel thermocouple	AG	Absolute gauge
4	Adsorber bomb	9	Digital recorder		
5	Water bath	10	Vacuum pump		

Fig (1) Schematic diagram of apparatus used for adsorption equilibrium measurement

The volume of the reservoir and the adsorber (together with the Swagelock fittings) and the other sections of the system were measured manometrically using nitrogen gas. Section C was charged with nitrogen gas to a known pressure P_1 = 2.5 MPa. Valve 5 was connected to a standard known volume previously evacuated cylinder vessel V_1 = 1 liter and opened until equilibrium was reached with a new pressure P_2, then the volume of section C was determined by the ideal gas equation of state:

$$V_C = \frac{P_2 V_1}{P_1 - P_2} \tag{1}$$

The volume of section A and B were determined in the same manner.

The granular adsorbent (10 g) was packed into the adsorption vessel and degassed for overnight under vacuum at a pressure of less than 3 Pa to clean the adsorbent. This pretreatment enabled us to make adsorption measurements without changing the adsorbent. After the adsorbent had been regenerated, the vacuum pump was switched off. The water bath with electrical stirrer thermo–stated hot plate was switched on until constant temperature was reached.

The procedure for measuring equilibrium adsorption was as follow:

1. Section A and C were pressurized with the adsorbate, corresponding to a pressure P_3 then the number of moles of the adsorbate was estimated according to the relation:

$$n_1 = \frac{P_3\left(V_C + V_A\right)}{RT} \tag{2}$$

Passage of gas to section B was allowed until equilibrium ($\Delta P \leq 3$ kPa/h). The equilibrium pressure was recorded as P_4.

2. Adsorber was isolated from the system. The number of moles of the adsorbate was estimated according to the relation:

$$n_2 = \frac{P_4\left(V_C + V_A + V_B\right)}{RT} \tag{3}$$

The amount adsorbed of the adsorbate at partial pressure equal to P_4 is determined according to a material balance equation:

$$q = \frac{n_1 - n_2}{W} \tag{4}$$

RESULTS & DISCUSSIONS

The partial pressure and temperature ranges were chosen for each component in viewing to the expected values in the natural gas and oil well effluent properties and component vapor pressure, which almost must be greater than the component partial pressure under specified temperature, to avoid condensation of gases on the adsorbent.

The experimental results for single gas equilibrium were fitted with Langmuir and Freundlich equations. BET and other equations that represent multi–layer adsorption were excluded because it is unlikely that multi–layer adsorption could have occurred in this study were all temperatures above the critical (Yang & Saunders, 1985).

The Langmuir equation takes the form:

$$\frac{q}{q_m} = \frac{BP}{1+BP} \tag{5}$$

The coefficients B and q_m depend on temperature in accordance to the following equations:

$$q_m = a_1 T^{a_2} \tag{6}$$

$$B = a_3 e^{a_4/T} \tag{7}$$

The Freundlich equation takes the form:

$$q = k_F P^{n_F} \tag{8}$$

The coefficients k_F and n_F depend on temperature in accordance to the following equations:

$$k_F = b_1 T^{b_2} \tag{9}$$

$$n_F = b_3 + b_4/T \tag{10}$$

The objective function (average relative error) used in the minimization routine was defined as:

$$E = \frac{1}{N}\sqrt{\sum_{i=1}^{N}\left(\frac{q_{i,exp} - q_{i,cal}}{q_{i,exp}}\right)^2} \tag{11}$$

where N is the number of experimental points and $q_{i,exp}$ and $q_{i,cal}$ are the experimental and calculated values of q_i, respectively.

The calculated constants for the two model equations along with the average relative error values were presented in table 1. The table shows that Langmuir equation correlates the experimental data with mean average relative error of 1.59% while 2.29% for Freundlich equation. Therefore, the best fit was achieved with Langmuir equation. The experimental equilibrium data was correlated by Langmuir equation and presented in figures 2 and 3.

Table (1) Summary of single gas adsorption isotherms results

Adsorbate	a_1	a_2	a_3	a_4	E %
CO_2	4.71×10^{-1}	-0.86	2.27×10^{-4}	999.67	2.67
CH_4	8.25×10^{-1}	-0.99	3.24×10^{-7}	705.96	0.51

Adsorbate	b_1	b_2	b_3	b_4	E %
CO_2	2.99×10^{-3}	-0.19	3.12×10^{-2}	180.99	2.80
CH_4	4.21×10^{-44}	15.42	-8.7×10^{-1}	385.45	1.77

All curves for any specified gas are similar in shape and are of the classic adsorption isotherm form. However, it was concluded that the strength of adsorption for CO_2 is greater than for CH_4, since it was recognized that CO_2 has isotherms with greater slopes at $P \rightarrow 0$, which indicates that the affinity for adsorption of CO_2 is greater than for CH_4.

The results also indicate that there is a fair correlation for the amount of adsorption on an adsorbent correspond to increased adsorption with higher gas molecular weight or critical temperature. This result is in agreement with published works (Lewis et al., 1950). Also, vapor pressure can be expected to be the predominant factor favoring adsorption. The much less volatile gas is more likely to condense on the surface since it has a much larger relative saturation value (P / P^*) than the more volatile one. This result was verified by several authors (Hyun & Danner, 1982).

Adsorption isotherms for the CH_4 and CO_2 gases on 5A molecular sieve at moderate temperature ranges are presented in figures 2 and 3. The marked decrease in adsorption with increasing temperature is obvious from these diagrams.

The heat of adsorption (ΔH) was calculated by application of the Clausius–Clapeyron equation (Smith, 1988) at neighboring temperatures. When this equation is applied to the two phase system of gas and adsorbed component on the surface, we get:

$$\left(\frac{dP}{dT}\right)_{\theta} = \frac{\Delta H}{T\left(V - V_a\right)} \qquad (12)$$

where V and V_a are the volumes per mole of adsorbed component in the gas and on the surface, respectively. V_a is very small and could be neglected. By assuming the ideal gas law for V we get:

$$\Delta H = -R\left(\frac{d\,ln P}{d\,1/T}\right)_{\theta} \qquad (13)$$

Table 2 shows the results of this equation.

Table (2) Heat of adsorption and condensation for gases

Component	ΔH, (kJ mole^{-1})	ΔH_{cond} at BP (kJ mole^{-1})
CH_4	14.804	8.180
CO_2	37.218	Sublimes at 195 K

In both cases the heats of adsorption are higher or expected to be higher than the latent heats of condensation but are low enough to be characterized as physical adsorption.

CONCLUSIONS

1. Equilibrium isotherms for single component adsorption of methane and carbon dioxide on 5A molecular sieve can be correlated by Langmuir equation.
2. The strength of adsorption for carbon dioxide is greater than for methane on 5A molecular sieve.

3. The heat of adsorption for both methane and carbon dioxide on 5A molecular sieve always greater than the latent heat of condensation.

NOMENCLATURE

$a_1,.., a_4$	Langmuir isotherm coefficients	-
$b_1,.., b_4$	Freundlich isotherm coefficients	-
k_F	Constant in Freundlich equation	Pa^{1-nF}
n	Number of moles	mole
n_F	Parameter in Freundlich equation	-
q	Adsorbed phase concentration	mole g^{-1}
y	Mole fraction in gas phase	-
B	Adsorption coefficient in Langmuir equation	Pa^{-1}
E	Average relative error	-
N	Number of experimental points	-
P	Pressure	Pa
$P*$	Vapor pressure	Pa
R	Ideal gas constant	J $mole^{-1}$ K^{-1}
T	Temperature	K
V	Volume	m^3
W	Mass of adsorbent	g
θ	Fraction of surface coverage	-
ΔH	Heat of adsorption	J $mole^{-1}$

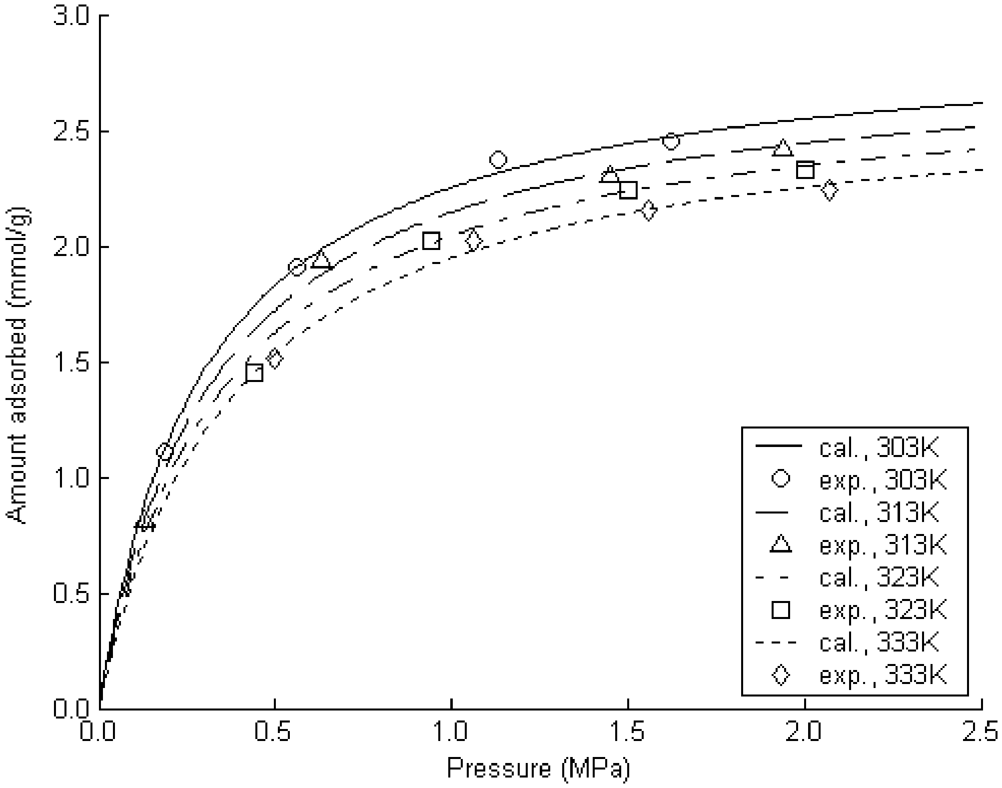


Figure (2) Adsorption equilibrium isotherms for the system Methane-5A Molecular sieve

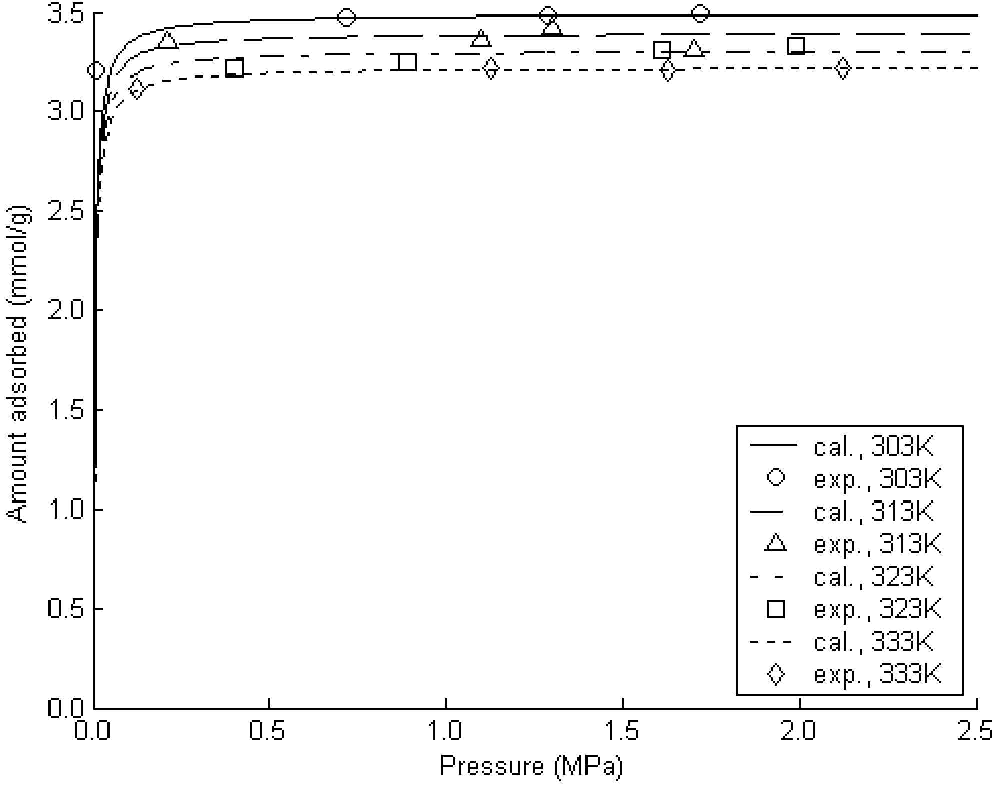


Figure (3) Adsorption equilibrium isotherms for the system Carbon dioxide-5A Molecular sieve correlated with Langmuir equation

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