

Experimental and theoretical studies of equilibrium isotherms for pure light hydrocarbons adsorption on 4A zeolite

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Abstract—Experimental and theoretical studies were reported on equilibrium isotherms of pure methane and ethane adsorption on 4A molecular sieve zeolite at 301 K. The experimental equilibria data were measured using the constant-volume method. The Langmuir, the Freundlich, and BET equations were used to fit the pure component experimental data. The results show that both the Langmuir and Freundlich equations correlated the pure component experimental data fairly well with a correlation coefficient of 0.998 and 0.977 for methane and ethane, respectively. The results of this study showed that ethane was more selectively adsorbed than methane on 4A molecular sieve zeolite.

Key words: Equilibrium Isotherm, Adsorption, 4A Molecular Sieve Zeolite, Methane, Ethane, Light Hydrocarbons

INTRODUCTION

The light hydrocarbon system such as methane and ethane is of ever growing interest because these components appear together in many petroleum gases such as natural gas, deethanizer or depropanizer overhead mixtures. The adsorption separation processes have been largely employed to recover these components with high purities. In the design and optimization of adsorption processes basic experimental equilibria data usually in the form of an adsorption isotherm are required [1].

An adsorption isotherm for a single gaseous adsorptive on a solid is the function which relates at constant temperature the amount of substance adsorbed at equilibrium to the pressure or concentration of the adsorptive in the gas phase. This isotherm is useful for indicating the affinity of an adsorbate for a particular adsorbent and to determine the adsorption capacity, which is of paramount importance to the capital cost, because it indicates the amount of adsorbent required, which also fixes the volume of the adsorber vessels. There are different types of adsorption isotherms as classified by the international union of pure and applied chemistry IUPAC; these isotherms can have very different shapes depending on the type of adsorbent, the type of adsorbate, and the intermolecular interactions between the gas and the surface [2].

There are three experimental methods generally used for measuring equilibrium adsorption isotherms, the volumetric method, the gravimetric method, and chromatographic method. The volumetric method is probably the best in terms of flexibility, reasonable accuracy, and low cost, as compared with the other methods [3].

Several theoretical equations have been used to correlate experimental equilibrium isotherm data for adsorption of pure gases on

solids such as the Langmuir isotherm, the Freundlich isotherm, and the BET isotherm. The Langmuir isotherm has been successfully used to describe adsorption equilibria of light hydrocarbons on molecular sieve zeolite [4].

The study of equilibrium isotherm for the adsorption of light hydrocarbons on different adsorbents has been an important subject for many investigators. Zhu et al. [5] studied the equilibrium isotherm of methane, ethane, propane, n-butane, and i-butane on silicalite-1. Newalkar et al. [6] used the volumetric method to measure the adsorption isotherm of methane, ethane and propane on hexagonal mesoporous silica. They used both the Langmuir and Langmuir-Freundlich isotherms to fit the data. Walton et al. [7] studied the adsorption isotherm of methane, ethane and n-butane on activated carbon using the gravimetric method. Grande et al. [8] used 4A zeolite to study the adsorption isotherm of pure propane and propylene at the temperatures of 423 and 473 K. Also, da Silva and Rodrigues [9] studied the adsorption equilibria for propylene and propane over 4A and 13X molecular sieve zeolite. Wender et al. [10] studied the adsorption isotherm of n-alkanes such as n-butane on NaY molecular sieve zeolite using the gravimetric method.

The aim of this investigation is to study experimentally and theoretically the equilibrium isotherms of pure methane and ethane adsorption on 4A molecular sieve zeolite.

EXPERIMENTAL WORK

1. Materials

1-1. Adsorbates

Methane and ethane (supplied by State Enterprise for Petrochemical Industries) of purity higher than 99.5% were used as adsorbates.

1-2. Adsorbent

4A molecular sieve zeolite (supplied by Lap orate Industries Ltd.) of particle density 1,352 g/l and an average particle size 0.09 cm³

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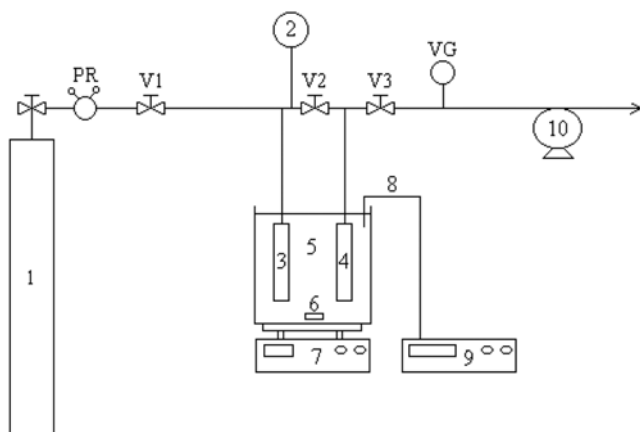


Fig. 1. Schematic diagram of equilibrium isotherm measurement apparatus.

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|-------------------------------|--------------------------------|
| 1. Gas cylinder | 8. Chromel-alumel thermocouple |
| 2. Heise pressure gauge | 9. Digital recorder |
| 3. Reservoir chamber | 10. Vacuum pump |
| 4. Adsorber chamber | V. Manual valve |
| 5. Water bath | PR. Pressure regulator |
| 6. Stir bar | VG. Vacuum gauge |
| 7. Magnetic stirrer hot plate | |

was used as adsorbent.

2. Apparatus

The apparatus, outlined in Fig. 1, is comprised of two iron pressure vessels connected together by (0.24 cm I.D. and 0.32 cm O.D.) stainless steel tubing. Both the reservoir and adsorption chambers have 0.02 l volume. The gas pressure was measured by a Heise bourdon gauge with a diameter of 43 cm and a pressure range from 0–6,891 kPa. A water bath was employed to provide a constant temperature environment for both the reservoir and the adsorber. The bath was thermostated and vigorously mixed by using a magnetic stirrer thermostat hot plate (Gallenkamp). The temperature of the bath was continuously measured and recorded by a digital recorder (Dacq TR-2721) and a thermocouple wire, calibrated with mercury thermometer. Both chambers were evacuated by (Leybold-Heraeus D8A) vacuum pump and (Acco Helicoids) gauge pressure prior to each experiment. The feed supplied from the cylinder was regulated by (Victory) pressure regulator.

3. Experimental Procedures

The activated adsorbent (10 g) was packed into the adsorption vessel and the apparatus, as shown in Fig. 1, was evacuated to less than 3 pa for three hours. This pretreatment, prior to each equilibrium measurements, enabled us to make adsorption measurements without changing the adsorbents. After the adsorbent had been regenerated, the vacuum pump was switched off. The water bath with electrical stirrer thermostated hot plate was set at the desired temperature of adsorption 301 K.

Pure gas was introduced into the reservoir vessel through valve V_1 until the desired concentration was reached. Valve V_1 was then closed and the initial concentration C_{ri} recorded when steady. Then valve V_2 was opened and the system allowed reaching equilibrium to record final concentration C_{rf} .

The amount of gas adsorbed at equilibrium q was determined from a mass balance. The amount of a component in the reservoir

vessel before adsorption is equal to the amount remaining in this vessel after adsorption plus the amount in the gas phase in the adsorber vessel plus the amount adsorbed in the adsorber vessel, then:

$$q = \frac{(C_{ri} - C_{rf})V_r - (C_{rf}\epsilon_o V_a)}{W} \quad (1)$$

The overall bed void fraction ϵ_o was determined by measuring the methanol volume V_1 required to fill the cylinder volume V_c packed with the zeolite weight W , then:

$$\epsilon_o = \frac{V_1}{V_c} \quad (2)$$

MATHEMATICAL MODEL

Langmuir, Freundlich, and BET equations were used to correlate experimental equilibrium isotherms data for pure components. These equations can be written as follows:

Langmuir isotherm

$$q = \frac{q_m BC}{1 + BC} \quad (3)$$

Freundlich isotherm

$$q = KC^n \quad (4)$$

BET isotherm

$$q = \frac{q_m K_B \left(\frac{C}{C^*} \right) \left(1 - \frac{C}{C^*} \right)}{\left[\left(1 + (K_B - 1) \frac{C}{C^*} \right) \right]} \quad (5)$$

A nonlinear least-squares regression program based on Gauss-Newton method was used to fit Eqs. (3)–(5) to experimental equilibrium isotherms data. This program gave the parameters of each equation and the agreement between experimental and calculated adsorption isotherms in terms of correlation coefficient.

RESULTS AND DISCUSSION

The experimental equilibrium data for pure methane and ethane adsorption on 4A molecular sieve zeolite, calculated from Eqs. (1) and (2), are fitted with Langmuir, Freundlich, and BET equations. The calculated constants for the three isotherms equations along

Table 1. Pure component equilibrium isotherm results

Pure component isotherm results correlated with Langmuir equation			
Adsorbate	q_m	B	C. Coef.
Methane	1.296880	0.024746	0.998
Ethane	2.548656	0.090584	0.997
Pure component isotherms results correlated with Freundlich equation			
Adsorbate	K	n	C. Coef.
Methane	0.098401	0.499074	0.987
Ethane	0.650195	0.291726	0.994
Pure component isotherms results correlated with BET equation			
Adsorbate	q_m	K_B	C. Coef.
Methane	2.581288	8836.53	–2.125
Ethane	4.564225	8710.07	–3.264

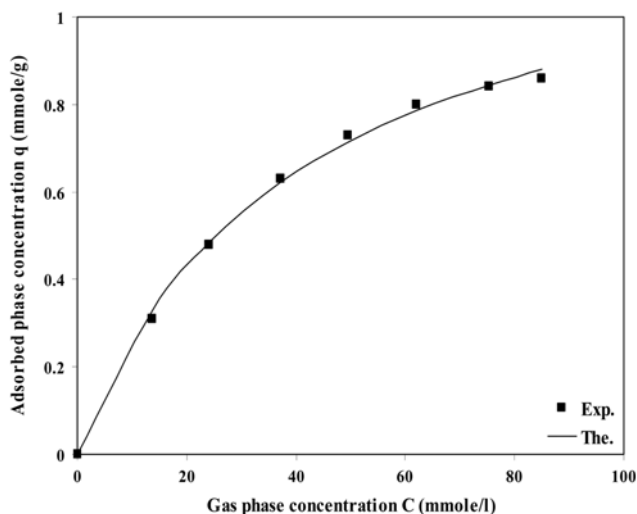


Fig. 2. Equilibrium isotherm of pure methane adsorption on 4A MSZ at 301 K correlated with Langmuir equation.

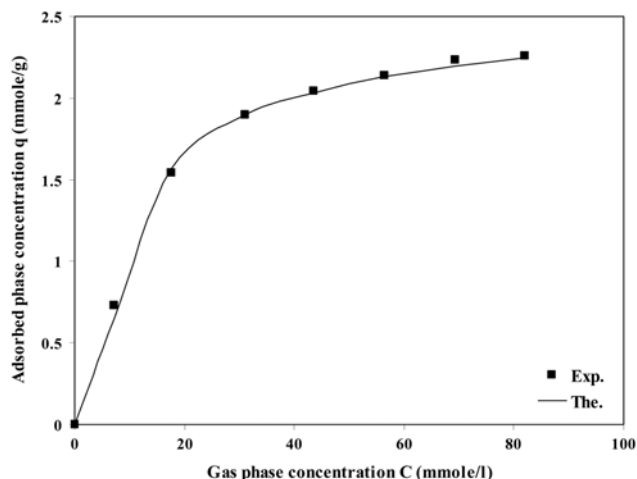


Fig. 3. Equilibrium isotherm of pure ethane adsorption on 4A MSZ at 301 K correlated with Langmuir equation.

with the correlations coefficients values are presented in Table 1.

This table shows that the Langmuir equation correlates with a correlation coefficient of 0.998 and 0.997 for methane and ethane, respectively. While the Freundlich equation correlates with correlation coefficient of 0.987 and 0.994 for methane and ethane, respectively. The BET equation correlates with a correlation coefficient of -2.125 and -3.264 for methane and ethane, respectively. Although, the Langmuir and Freundlich equations give good fitting, the best fit is achieved with the Langmuir equation. Thus, the experimental equilibrium data is correlated by the Langmuir equation and presented in Figs. 2 and 3.

These figures show that the maximum loading of ethane on 4A zeolite is 2.5 mmole/g while that of methane is 1.3 mmole/g, which means that ethane is more selectively adsorbed than methane on 4A molecular sieve zeolite. This is in agreement with Song et al. [4] who showed that at a given concentration and temperature, the amount of the adsorbed hydrocarbon component increased with molecular weight. The study of the equilibrium isotherm indicates

that the adsorption capacity increases with increasing the inlet concentration of the adsorbate, but it reaches nearly a steady value at high concentration. This means that the equilibrium is of the favorable type.

The above results are also observed by Pakseresht et al. [11] who showed that the equilibrium isotherm data for adsorption of pure methane on 5A molecular sieve zeolite could be fitted by the Langmuir isotherm with good correlation coefficient. Different researchers showed that both the Langmuir and Freundlich equations succeeded to simulate pure component adsorption isotherms in different molecular sieve zeolites [12]. These results are not surprising because the BET isotherm deals with multilayer adsorption, while the Langmuir and Freundlich isotherm deal with monolayer adsorption, such as in zeolites.

CONCLUSIONS

1. Experimental equilibrium isotherm data for pure component adsorption showed that 4A molecular sieve zeolite had more affinity with ethane than methane at the studied temperature.
2. Equilibrium isotherms for the pure component adsorption of methane and ethane on 4A molecular sieve zeolite were fitted successfully by both the Langmuir and Freundlich equations.

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NOMENCLATURE

Notation

- B : Langmuir equation coefficient [//mmole]
 BET : Brunauer, Emmet, and Teller
 B_{ij}, B_{ij} : modified extended Langmuir equation coefficients [//mmole]
 C : gas phase concentration [mmole/l]
 IUPAC : international union of pure and applied chemistry
 K : Freundlich equation coefficient [$l^n/\text{mmole}^{n-1} \cdot \text{g}$]
 K_B : BET equation coefficient
 K_{ij} : extended Freundlich and Sheindorf equations coefficient
 MSZ : molecular sieve zeolite
 n : Freundlich equation parameter
 n_{ij}, n_{ij} : Fritz and Extended Freundlich equations parameters
 q : adsorbed phase concentration [mmole/g]
 V : volume [l]
 W : mass of adsorbent [g]
 ϵ_o : over all bed void fraction

Subscripts

- a : adsorber vessel
 c : cylinder
 i : component i
 j : component j
 l : methanol
 m : mono-layer
 n : component n
 r : reservoir vessel

- rf : final condition of reservoir vessel
 ri : initial condition of reservoir vessel
 * : saturation condition

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