Prediction of breakthrough curves for light hydrocarbons adsorption on 4A molecular sieve zeolite

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Abstract−Breakthrough curves for the adsorption of methane, ethane, and propane mixture on 4A molecular sieve zeolite were obtained experimentally and theoretically at a constant temperature of 301 K. The equilibrium model and linear driving force model were used to predict the experimental breakthrough curves for this multi component mixture. The equilibrium model gave a satisfactory fit for experimental data. The model equations were solved by a numerical method based on backward finite difference with a fixed griding technique. The effect of feed flow rate (0.385-3.465 *l/* min), feed concentration (60.72-182.16 mmole/*l*), and adsorbates composition (11.73-20.11%) on the breakthrough curves were examined.

Key words: Breakthrough Curves, 4A Molecular Sieve Zeolite, Light Hydrocarbons, Equilibrium Model, Multi Component Adsorption

INTRODUCTION

A light hydrocarbon system such as methane, ethane, and propane system 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 kinetic data usually in the form of a breakthrough curve are required [1].

The breakthrough curve for an adsorbed component in a fixed bed column is the relation between the ratio of effluent concentration to influent concentration of the component and the time or throughput volume. The dynamic behavior of a fixed bed column is described in terms of this curve. The shape of this curve is determined by the shape of the equilibrium isotherm and is influenced by the individual transport processes in the column and in the adsorbent. The most efficient adsorption performance will be obtained when the shape of the breakthrough curve is as sharp as possible [2].

To describe the observed breakthrough curve behavior a mathematical models are needed. The most commonly used models are the equilibrium model in which the equilibrium between the gas and solid phases is assumed to be established with no mass transfer resistance [3] and the linear driving force model in which the effects of mass transfer resistances are included [4].

To develop a mathematical model it is necessary to set up and solve the set of coupled partial differential equations which describes the dynamic behavior of the system. Basically, three types of numerical approaches have been used for numerical simulations of the multi component adsorption: the method of characteristics, the method of orthogonal collocation, and the finite difference method. The finite difference methods are frequently utilized due to their simplicity, efficiency in solving hyperbolic and parabolic equations, and easy of varying initial and boundary conditions. These methods can be categorized into explicit and implicit methods. The explicit method is simple and needs no iteration as compared with the implicit method [5].

The study of breakthrough curves for the adsorption of light hydrocarbons on different adsorbents has been an important subject for many investigators. Prasetyo and Do [6] studied the breakthrough curves for the adsorption of methane, ethane, propane, and n-butane on activated carbon. Heyden et al. [7] examined the effect of mass transfer resistance on the breakthrough curves for the adsorption of a feed stream consisting of equimolar fractions of methane and ethane on carbon nanotubes. Grande et al. [8] studied the breakthrough curves for the adsorption of propane and propylene on 4A molecular sieve zeolite.

The aim of the present investigation is to study experimentally and theoretically the breakthrough curves of methane, ethane, and propane mixture on 4A molecular sieve zeolite, and the effect of the feed flow rate, feed concentration, and the adsorbates composition on breakthrough curves.

EXPERIMENTAL WORK

1. Materials
1-1. Adsorbates
Pure methane, pure ethane and three gaseous mixtures of methane,

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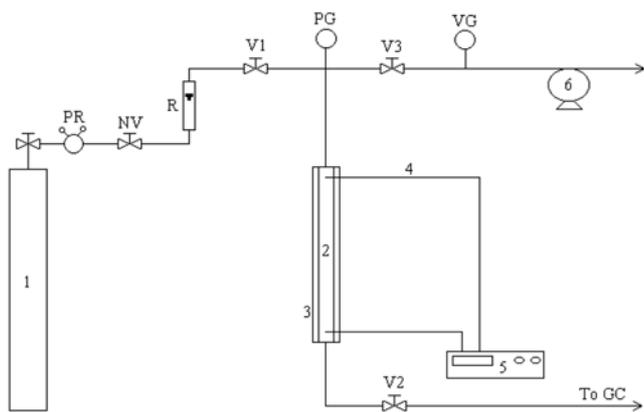
Fig. 1. Schematic diagram of adsorption kinetics measurement apparatus.

1. Feed cylinder	V. Manual valve
2. Adsorption column	PR. Pressure regulator
3. Glass wool insulator	PG. Pressure gauge
4. Termocouples	NV. Needle valve
5. Digital recorder	VG. Vacuum gauge
6. Vacuum pump	R. Rotameter

ethane, and propane were used as adsorbates. Methane and ethane (Supplied by State Enterprise for Petrochemical Industries) were of purity higher than 99.5%. The compositions of the three gaseous mixtures (supplied by Al-Durra Refinery) were 3.81%, 7.92%, and 88.27%; 5.17%, 10.75%, and 84.08%; 6.53%, 13.58%, and 79.89%, respectively.

1-2. Adsorbent

4A molecular sieve zeolite (supplied by Lap orate Industries Ltd) was used as adsorbent.

1-3. Auxiliaries

Nitrogen (supplied by Al-Mansour Factory) of purity greater than 99% was used as a carrier gas of gas-solid chromatography analyzer.

2. Apparatus

A schematic diagram of the apparatus is shown in Fig. 1. The adsorption column was a stainless steel (type CF-8M) pipe 66 cm long and 3.3 cm I.D. Gauze plate of fine mesh and thin layer of glass wool were placed at both ends of the bed to hold packing in position and prevent heat loss from column ends. All tubing was (0.24 cm I.D. and 0.32 cm O.D.) stainless steel. A layer of insulation (glass wool) covered the column in order to make the temperature gradient in the radial direction as small as possible. The insulation also simulated adiabatic operation. The inlet and outlet gas temperature were measured and recorded at the beginning as well as at the end of each experiment by multi-channel digital recorder (Dacq TR-2721). This was done by two finely calibrated thermocouples (0.16 cm) sheathed in a (0.32 cm) copper protection tube inserted in the center of the packed column. The inlet gas flow rate was controlled by a needle valve (Micro Hooke mite) and measured by a rotameter (GEC-Elliott). The gas composition was measured by a gas-solid chromatography (GC) unit consisting of a thermal conductivity detector (TCD) (Varian vista 6000), integrator (Packard 602), and recorder (Packard 621). The GC carrier gas flow rate was measured by soap film wet flowmeter.

3. Experimental Procedure

A weighed sample of activated adsorbent was placed in the ad-

sorption column and degasified by evacuation to a pressure less than 3pa for three hours. After the adsorbent was regenerated, the vacuum pump was switched off. Then the feed (influent gas) was introduced through valve V_1 into the adsorption column. The influent gas pressure or concentration was measured by pressure regulator and its inlet flow rate was controlled and measured by a needle valve and rotameter, respectively. Samples from effluent stream of the adsorption column were analyzed periodically (each 1 min) until breakthrough of all the adsorbate species was complete. The inlet and outlet temperature were measured at the beginning as well as at the end of each experiment.

4. Densities and Void Fractions Calculation

The bed density ñ_b was determined by measuring the weight W of molecular sieve required to fill the volume V_c of cylinder:

$$\rho_b = \frac{W}{V_c} \tag{1}$$

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

$$\varepsilon_o = \frac{V_1}{V_c} \tag{2}$$

MATHEMATICAL MODEL

1. Pure Component Adsorption Isotherm

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

Langmuir Isotherm

$$q = \frac{q_m BC}{1 + BC} \tag{3}$$

Freundlich Isotherm

$$q = KC^n \tag{4}$$

A nonlinear least-squares regression program based on Gauss-Newton method was used to fit Eqs. (3) and (4) to experimental equilibrium isotherm data. This program gave the parameters of each equation and the agreement between experimental and calculated adsorption isotherms in terms of correlation coefficient. The calculated constants for the two isotherms equations along with the

Table 1. Pure component adsorption 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
Propane	0.342858	0.010547	0.992
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
Propane	0.007121	0.710583	0.981
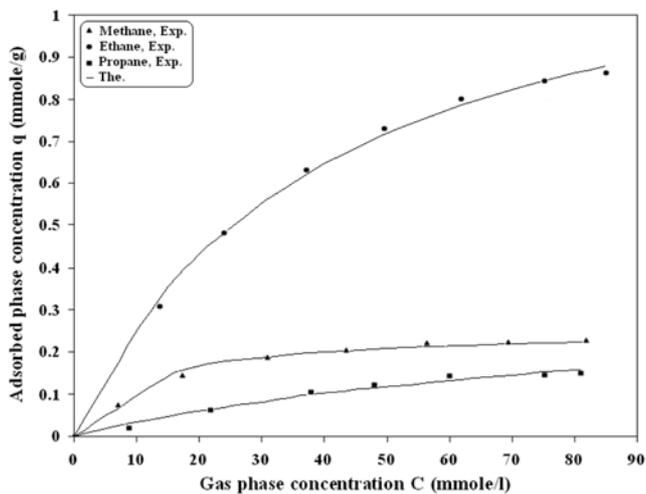
Fig. 2. Adsorption equilibrium isotherm of pure methane, ethane and propane on 4A MSZ at 301 K correlated with Langmuir equation.
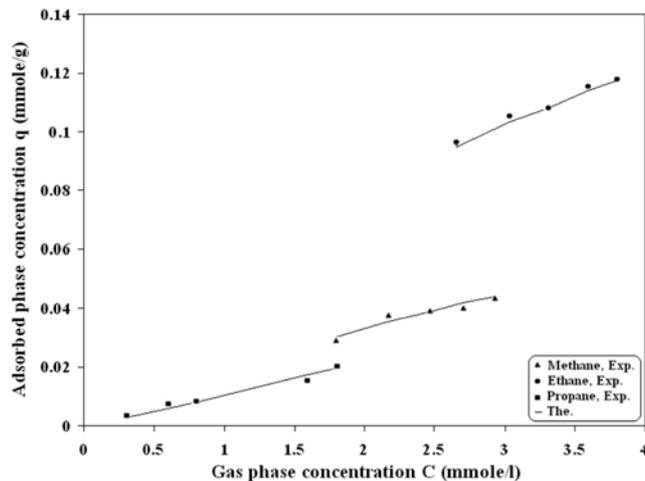
Fig. 3. Adsorption equilibrium isotherm of multi component mixture ($3.81\%CH_4$, $7.92\%C_2H_6$, $88.27\%C_3H_8$) on 4A MSZ at 301 K correlated with extended Freundlich equation.

correlations coefficients values are presented in Table 1.

This table shows that the best fit is achieved with the Langmuir equation. Thus, the pure component experimental equilibrium data for methane, ethane and propane, taken from Grande et al. [8], is correlated by the Langmuir equation and presented in Fig. 2.

2. Multi Component Adsorption Isotherms

To correlate experimental equilibrium isotherms data for multi components, modified extended Langmuir and extended Freundlich equations were used. These equations can be written as follows:

Modified extended Langmuir Isotherm

$$q_i = \frac{q_{mi}B_{ii}C_i}{1+\sum_{j=1}^{n}B_{ij}C_j} \tag{5}$$

Extended Freundlich Isotherm

$$q_i = \frac{K_iC_i^{n_i+n_{ii}}}{\sum_{j=1}^{n}K_{ij}C_j^{n_{ij}}} \tag{6}$$

A nonlinear least-squares regression program based on the Gauss-Newton method was used to fit Eqs. (5) and (6) to experimental equilibrium isotherm data. This program gave the parameters of

each equation and the agreement between experimental and calculated adsorption isotherms in terms of correlation coefficient. The calculated constants for the two isotherm equations along with the correlation coefficient values are presented in Table 2. This table shows that the extended Freundlich equation give a best correlation. Thus, the multi component experimental equilibrium data is correlated by the extended Freundlich equation and presented in Fig. 3.

3. Effluent Concentration Calculation

The present system is a fixed bed adsorber packed with porous cylindrical adsorbent particles that are subjected to a feed gas at the ambient temperature. To predict the breakthrough curves of this system, a mathematical model is developed on the basis of the following assumptions:

1. Isothermal operation based on experimental observation of 1 K maximum temperature swing.

2. Pressure drop through the adsorbent bed is negligible; therefore, the velocity and density of the fluid are constant.

3. The ideal gas law is obeyed based on a maximum used pressure of 4.5 atm.

4. The velocity profile is flat and longitudinal dispersion is insignificant.

Table 2. Multi component adsorption isotherm results for ($3.81\%CH_4$, $7.92\%C_2H_6$, $88.27\%C_3H_8$) mixture

Multi component isotherm results correlated with extended Freundlich equation								
Adsorbate	K_i	n_i	K_{i1}	K_{i2}	K_{i3}	n_{i1}	n_{i2}	n_{i3}	C. Coef.
Methane	0.098	0.499	1	0.002	5.16	0.738	4.52	0.044	0.999
Ethane	0.650	0.291	14.08	1	0.05	0.209	0.69	3.187	0.999
Propane	0.007	0.710	−0.122	−0.224	1	1.700	−1.57	0.720	0.994

Multi component isotherm results correlated with modified extended Langmuir equation				
Adsorbate	q_{mi}	B_{i1}	B_{i2}	B_{i3}	C. Coef.
Methane	1.296	0.013	−0.037	0.086	0.998
Ethane	2.548	0.315	0.022	−0.089	0.994
Propane	0.342	0.916	−0.503	0.060	0.911

5. Gas phase concentration gradients in the radial direction are negligible.

6. Bed porosity is uniform.

7. The cylindrical adsorbent pellets can be modeled as spheres have the same external surface area to volume ratio.

Under the above assumptions, the governing equations and appropriate initial and boundary conditions can be written as follows:

Component i mass balance:

$$u_s\left(\frac{\partial C_i}{\partial z}\right) + \varepsilon_o\left(\frac{\partial C_i}{\partial t}\right) + \rho_b\left(\frac{\partial q_i}{\partial t}\right) = 0 \tag{7}$$

Initial and boundary conditions:

$$C_i \ (0 < z < L, \ t=0)=0 \tag{8}$$

$$q_i \ (0 < z < L, \ t=0)=0 \tag{9}$$

$$C_i \ (z=0, \ t>0)=C_I \tag{10}$$

An explicit backward finite difference method with fixed griding technique was used to approximate both the change of gas phase adsorbate concentration with axial position and time, then:

$$C_i(z,t) = \frac{\varepsilon_o C_i(z, t-\Delta t) + \frac{\Delta t}{\Delta z}u_s C_i(z-\Delta z, t) - \rho_b \Delta q(z,t)}{\varepsilon_o + \frac{\Delta t}{\Delta z}u_s} \tag{11}$$

The quantity adsorbed of component i within the adopted length and time increments can be calculated using either the equilibrium model or the linear driving force model, then:

Equilibrium model
$$\Delta q_i(z,t)=q_i(z-\Delta z,t)\Delta q_i(z,t-\Delta t) \tag{12}$$

LDF model
$$\Delta q_i(z,t)=K_{Gi}\,\Delta t(q_i(z-\Delta z,t)-q_i(z,t-\Delta t)) \tag{13}$$

By using the extended Freundlich equation to express the equilibrium isotherm, then:

$$q_i(z-\Delta z,t) = \frac{K_i C_i^{n_i+n_{ii}}(z-\Delta z,t)}{\sum\limits_{j=1}^{n} K_{ij} C_j^{n_{ij}}(z-\Delta z,t)} \tag{14}$$

$$q_i(z,t-\Delta t) = \frac{K_i C_i^{n_i+n_{ii}}(z,t-\Delta t)}{\sum\limits_{j=1}^{n} K_{ij} C_j^{n_{ij}}(z,t-\Delta t)} \tag{15}$$

The above set of equations was solved numerically with the aid of a FORTRAN computer program to give the effluent concentration distribution. Numerical values of the parameters employed in the calculations are listed in Table 3.

RESULTS AND DISCUSSION

Fig. 4 shows a comparison between the experimental and theo-

Table 3. Adsorption bed parameters used for computation

| Parameter	Source	Value
ρ_b (g/L)	Eq. (1)	730
ε_o	Eq. (2)	0.612
d (cm)	Direct	3.3
L (cm)	Direct	66
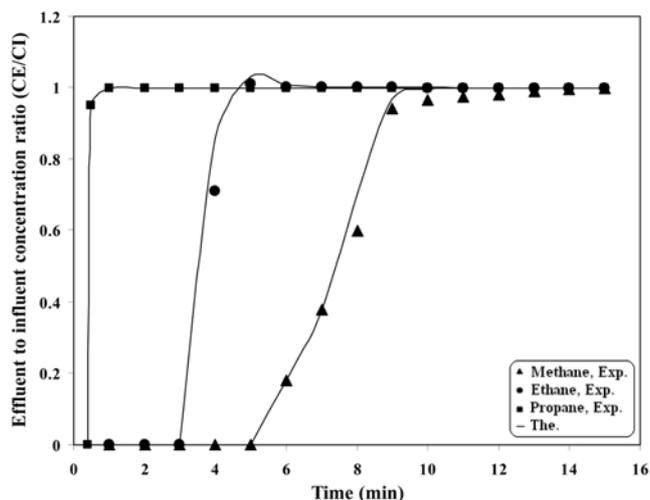
Fig. 4. Comparison of theoretical with experimental breakthrough curve for (3.81%CH$_4$, 7.92%C$_2$H$_6$, 88.27%C$_3$H$_8$) mixture at 80.96 mmole/l, 0.770 l/min, & 301 K.

retical breakthrough curves using the equilibrium model. The equilibrium model correlates the experimental breakthrough curve data of this figure with a correlation coefficient of 0.992, 0.985 and 0.980 for methane, ethane and propane, respectively. While the linear driving force model correlates with a correlation coefficient of 0.739, 0.705 and 0.685 for methane, ethane and propane, respectively. For the latter model the values of mass transfer parameter were 0.252 min^{-1}, 0.119 min^{-1} and 0.088 min^{-1} for methane, ethane and propane, respectively.

In this figure the non-key component (methane) moves more quickly than the key component (ethane) and is adsorbed on the fresh zeolite downstream of the bed. The non-key component is displaced or purged out from the adsorbent while the key component is being adsorbed in its place. Methane is considered as the non-key component, and ethane is the key component, while propane is slowly adsorbed and first appears in the effluent stream. The figure also shows that the rate of adsorption for methane is higher than for ethane. These observations are in agreement with Prasetyo and Do [6] who found that the adsorption rate decreased with the molecular weight of hydrocarbons in an exponential manner.

Initially, each component is adsorbed according to its individual diffusion rate and its concentration in the gas phase. In the initial stage no equilibrium is achieved. Thereafter, the process proceeds in such a way that the equilibrium is approached by mutual displacement, i.e., one of the components is desorbed again. The more selectively adsorbed component will displace the less one. This raises the fluid phase composition of the less selectively adsorbed component to such an extent that it rises to a peak composition above that of the inlet composition. The roll-up or overshoot phenomenon had also been demonstrated by Dexin and Youfan [9] for the adsorption of methane, ethane, and carbon dioxide mixture on 4A molecular sieve zeolite. Since ethane was more selectively adsorbed than carbon dioxide, and methane was less selectively adsorbed than carbon dioxide, carbon dioxide displaced methane, and ethane displaced carbon dioxide. The phenomenon had also been mentioned by Hu et al. [10] for binary adsorption system. This phenomenon can be
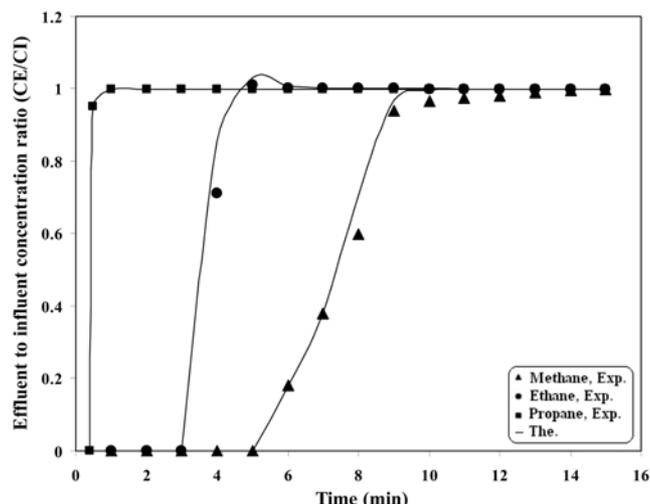
Fig. 5. Breakthrough curve for (3.81%CH$_4$, 7.92%C$_2$H$_6$, 88.27% C$_3$H$_8$) mixture on 4A MSZ at 0.770 *l*/min, 80.96 mmole/*l*, & 301 K.
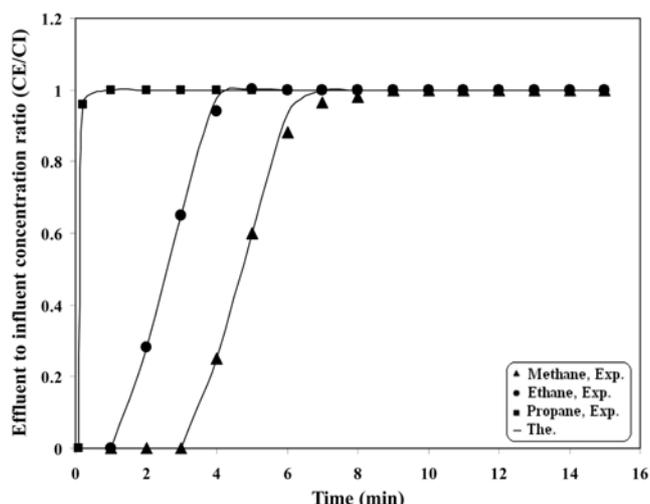

Fig. 7. Breakthrough curve for (3.81%CH$_4$, 7.92%C$_2$H$_6$, 88.27% C$_3$H$_8$) mixture on 4A MSZ at 2.888 *l*/min, 80.96 mmole/*l*, & 301 K.
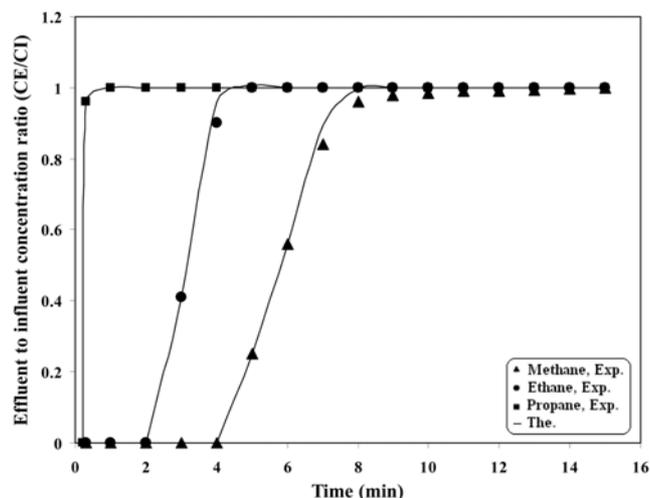
Fig. 6. Breakthrough curve for (3.81%CH$_4$, 7.92%C$_2$H$_6$, 88.27% C$_3$H$_8$) mixture on 4A MSZ at 1.733 *l*/min, 80.96 mmole/*l*, & 301 K.
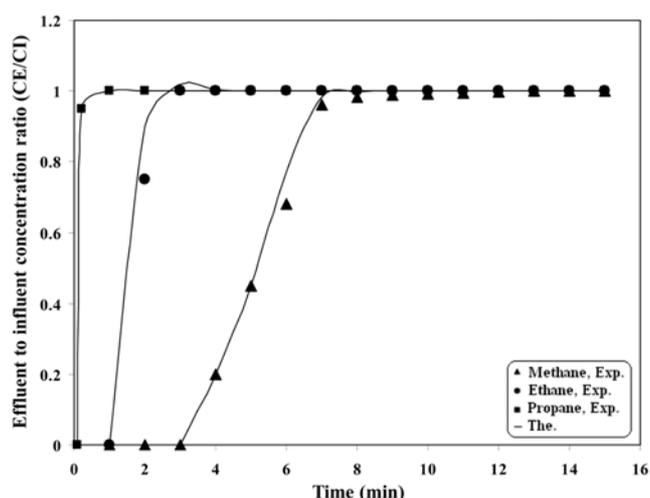
Fig. 8. Breakthrough curve for (3.81%CH$_4$, 7.92%C$_2$H$_6$, 88.27% C$_3$H$_8$) mixture on 4A MSZ at 80.96 mmole/*l*, 0.770 *l*/min, & 301 K.

taken advantage of in the separation of components by suppressing adsorption prior to breakthrough of the next component.

1. Effect of Feed Flow Rate

The effect of feed flow rate on the breakthrough curve of multi component mixture is shown in Figs. 4-6. These figures show that the breakthrough curves shifted towards the origin with increasing feed flow rate (velocity). When the flow rate is increased from 0.770 *l*/min to 2.888 *l*/min the time required for complete column saturation decreases from 12 min to 8 min for methane, and from 15 min to 10 min for ethane. In particular, a less sharp breakthrough curve is obtained at the highest flow rate tested, indicating poor utilization of the column capacity. The use of high flow rates reduces the time that adsorbates are in contact with the adsorbent, thus allowing less time for adsorption to occur, leading to an early breakthrough of adsorbates. However, it must be noted that the use of low flow rates will result in long overall processing times which

may not be desirable in practice when large volume feed have to be processed. According to Cooney [11], the tailing of a breakthrough curve (i.e., a slow approach of effluent to influent gas phase concentration ratio C_E/C_I towards 1) was commonly observed due to high influent flow rates.

2. Effect of Feed Concentration

The effect of feed concentration on the breakthrough curve of a multi component mixture is shown in Figs. 7-9. These figures show that the breakthrough curves shift away from the origin as the feed concentration increases. When the feed concentration increases, the concentration gradient (driving force) increases and equilibrium is achieved. In this case there will be high loading of adsorbates. This leads to a late breakthrough of adsorbates. These observations are in agreement with the results of Arumugam et al. [12] who showed that a lower adsorption capacity or loading would be realized during the adsorption step due to lowering in feed concentration.
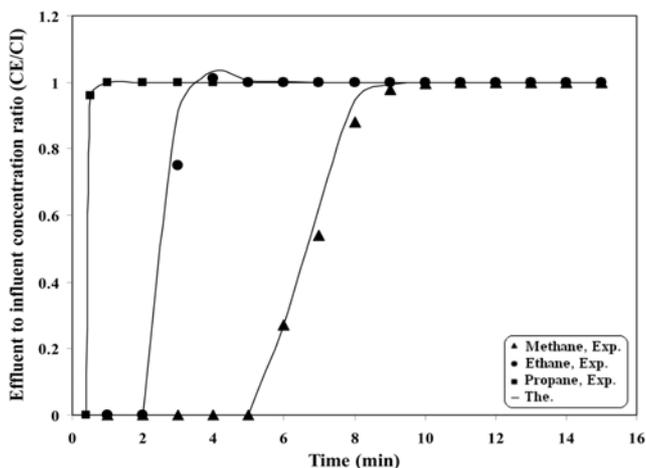
Fig. 9. Breakthrough curve for (3.81%CH$_4$, 7.92%C$_2$H$_6$, 88.27% C$_3$H$_8$) mixture on 4A MSZ at 121.44 mmole/*l*, 0.770 *l*/min, & 301 K.
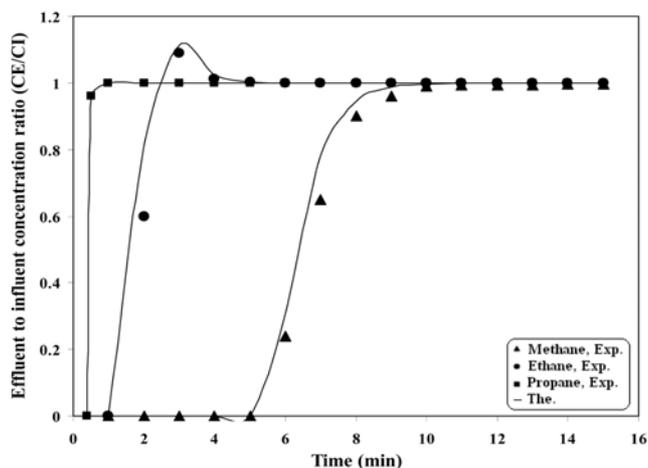

Fig. 12. Breakthrough curve for (5.17%CH$_4$, 10.75%C$_2$H$_6$, 84.08% C$_3$H$_8$) mixture on 4A MSZ at 0.770 *l*/min, 80.96 mmole/*l*, & 301 K.
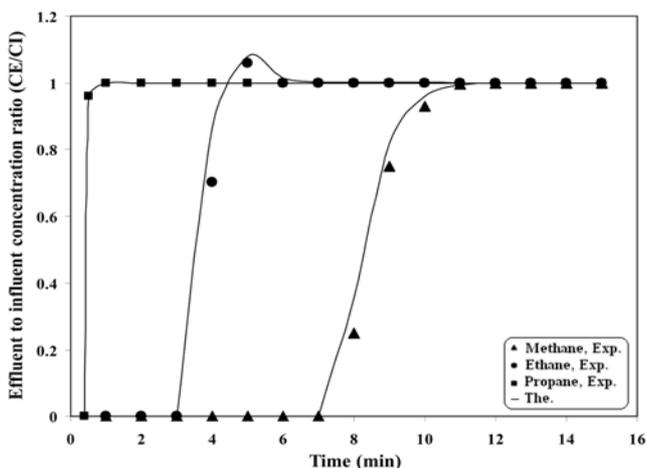
Fig. 10. Breakthrough curve for (3.81%CH$_4$, 7.92%C$_2$H$_6$, 88.27% C$_3$H$_8$) mixture on 4A MSZ at 161.92 mmole/*l*, 0.770 *l*/min, & 301 K.
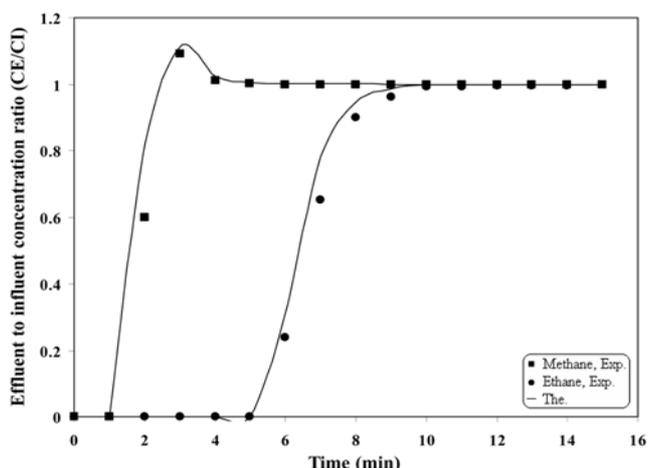
Fig. 13. Breakthrough curve for (6.53%CH$_4$, 13.58%C$_2$H$_6$, 79.89% C$_3$H$_8$) mixture on 4A MSZ at 0.770 *l*/min, 80.96 mmole/*l*, & 301 K.
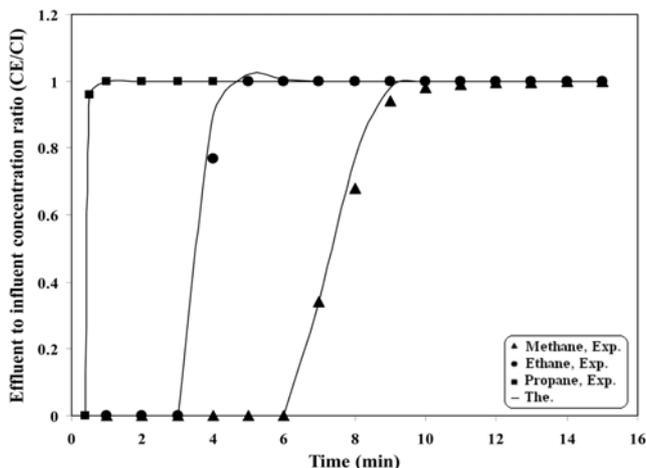
3. Effect of Adsorbate Composition

The effect of adsorbate composition on the breakthrough curve of a multi component mixture is shown in Figs. 10-13. These figures show that the breakthrough curves shift towards the origin as the adsorbate composition increases. An increase in the inlet concentration of ethane gives a higher roll-up and an early breakthrough of methane. This is because, at high adsorbate composition, ethane is adsorbed competitively and consequently more of methane is displaced. This displacement of methane is demonstrated by desorption of a proportion of this component during the period between its breakthrough and breakthrough of ethane. These observations are in agreement with that of Hu et al. [13] who studied the adsorption of ethane-propane mixture on activated carbon.

CONCLUSIONS

1. The overshoot phenomenon was observed for the less adsorbed component (methane) because of the displacement of the more ad-

Fig. 11. Breakthrough curve for (3.81%CH$_4$, 7.92%C$_2$H$_6$, 88.27% C$_3$H$_8$) mixture on 4A MSZ at 0.770 *l*/min, 80.96 mmole/*l*, & 301 K.

sorbed component (ethane).

2. The adsorption rate of ethane was more than that of methane and propane.

3. The equilibrium model was solved numerically by the finite difference technique, and it was found that this model succeeded in representing the experimental multicomponent breakthrough curves.

4. An increase in feed flow rate and adsorbates composition or a decrease in feed concentration gave an early adsorbate breakthrough.

ACKNOWLEDGMENT

NOMENCLATURE

Notation

B : Langmuir equation coefficient [l/mmole]

B_{ii}, B_{ij} : modified extended Langmuir equation coefficients [mmole/l]

C : gas phase concentration [mmole/l]

C_I : feed or influent gas phase concentration [mmole/l]

C_E : product or effluent gas phase concentration [mmole/l]

K : Freundlich equation coefficient [l^n/mmole^{n-1}·g]

K_i, K_{ij} : extended Freundlich equation coefficients

K_G : mass transfer parameter in linear driving force model [l/min]

n : Freundlich equation parameter

n_i, n_{ii}, n_{ij} : extended Freundlich equation parameters

q : adsorbed phase concentration [mmole/g]

t : time [min]

u_s : superficial gas velocity [cm/min]

V : volume [l]

W : mass of adsorbent [g]

z : axial coordinate (distance from the bed inlet) [cm]

ε_o : overall bed void fraction

ρ_b : bed density [g/l]

Δq : increment of adsorbed phase concentration [mmole/g]

Δt : increment of time

Δz : increment of distance

Subscripts

i : component i

c : cylinder

j : component j

l : methanol

n : component n

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