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A Novel Solution Method for Interpreting Binary Adsorption Isotherms from Concentration Pulse Chromatography Data

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Abstract. Adsorption separation of carbon dioxide from nitrogen (N_2, *which represents air*) was investigated by using H-ZSM-5 as the adsorbent with SiO_2/Al_2O_3 ratios of 30 and 280. Pure and binary isotherms at 40°C have been determined experimentally using concentration pulse chromatography.

Presently available methods for determining binary isotherms from concentration pulse chromatography data have been reviewed and shown incapable of interpreting this particular binary system. A novel solution method is presented and shown to be superior to the other methods.

The binary isotherms for the CO_2-N_2 system show an increase in CO_2 selectivity with increase in surface heterogeneity. The optimal separation factor for H-ZSM-5-30 was found to be 215 at 0.7% CO_2 in the feed, whereas, H-ZSM-5-280 has an optimal separation factor of 48 at 2.7% CO_2 in the feed.

Keywords: binary adsorption, concentration pulse method, adsorption of CO_2, adsorption of N_2, ZSM-5, separation of CO_2 and N_2

Introduction

The combustion of fossil fuels and deforestation have increased the concentration of greenhouse gases and upset the natural balance. Carbon dioxide (CO_2) is presently the most important greenhouse gas to control since it contributes over 50% of the known greenhouse effect. Separation technologies are needed to remove and use the CO_2 from industrial processes, thereby preventing the gas from entering the atmosphere (Farla et al., 1995).

The use of adsorption based gas separations for industrial processes are widespread. The developments of new adsorbents for these separations are also evolving rapidly. This growth facilitates the need to characterize the adsorbents for a very large subset of gases. One dynamic method of analysis is by use of the chromatographic technique. This method can be employed in several ways: tracer gas, step change, and pulse chromatography. In this study, concentration pulse chromatography has been employed (Van der Vlist and Van der Meijden, 1973; Shah and Ruthven, 1977; Hyun and Danner, 1982; Buffman et al., 1985, 1999; Tezel et al., 1992; Mason and Buffman, 1996; Heslop et al., 1996; Kabir et al., 1998).

The use of concentration pulse chromatography for adsorbent screening is very attractive since it is relatively inexpensive to setup and has a high turnover rate. However, presently available methods for determining binary isotherms from concentration pulse chromatographic data for highly selective adsorbents are not applicable, as shown in this study. A novel solution method using the K_p-functions proposed in the literature for determining the binary isotherms has been given and shown capable of interpreting highly selective binary systems.

Background and Literature Review

With concentration pulse chromatography, a pulse of sample is injected into the carrier stream and passes through an adsorbent packed column. The response of the column to the injection is measured as concentration vs. time at the exit of the column. From this response peak a mean retention time of the sample, μ, is determined experimentally:

$$\mu = \frac{\int_0^\infty c(t - \mu_D)\, dt}{\int_0^\infty c\, dt} \tag{1}$$

The term μ_D is the mean dead time. This dead time is the measure of the time required for a sample pulse to travel through the empty volume of the interconnecting tubing from injection point to the detector, and void space in the packed column.

At that carrier gas composition the mean retention time is related to the effective isotherm slope, K_p, by Eq. (2), (Shah and Ruthven, 1977, Van der Vlist and Van der Meijden 1973; Hyun and Danner, 1982; Buffman et al., 1985; Tezel et al., 1992; Triebe and Tezel, 1995; Heslop et al., 1996; Kabir et al., 1998):

$$\begin{gathered} \mu = \frac{L}{v}\left[1 + \frac{(1-\varepsilon)}{\varepsilon}K\right] \\ K_p(\text{Dimensional}) = K(\text{Dimensionless}) \cdot \text{CF} \end{gathered} \tag{2}$$

The system dependent constant CF is the conversion factor for transforming the dimensionless K to the dimensional K_p. The K_p value is related to the slopes of the isotherms of the components in the carrier gas mixture. For a binary mixture, the relationship is given as follows:

$$K_p(\text{Experimental}) = (1 - y_1)\frac{dq_1}{dP_1} + y_1\frac{dq_2}{dP_2} \tag{3}$$

where $\frac{dq_1}{dP_1}$ and $\frac{dq_2}{dP_2}$ are the slopes of the adsorption isotherms for components 1 and 2, respectively.

This method allows for the experimental evaluation of both pure and binary mixture isotherms when K_p values are determined for different concentrations of the carrier gas.

The interpretation for pure isotherms is performed if the second component in the carrier gas mixture is not appreciably adsorbed, for example when helium (He) is used. This results with $\frac{dq_2}{dP_2}$ in the second term of Eq. (3) being constant, D:

$$K_p(\text{Experimental}) = (1 - y_1)\frac{dq_1}{dP_1} + y_1 D \tag{4}$$

The value of D is determined from the limiting value of K_p as y_1 approaches 1. The pure component isotherm is then obtained by integration of Eq. (4) with the K_p determined for different concentrations of the carrier gas from Eqs. (1) and (2). (Schneider and Smith, 1968; Shah and Ruthven, 1977; Ruthven and Kumar, 1980; Hyun and Danner, 1982, 1985; Tezel et al., 1992; Triebe and Tezel, 1995; Kabir et al., 1998).

For binary isotherms, both components in the mixed carrier gas are adsorbed and $\frac{dq_2}{dP_2}$ in the last term of Eq. (3) is not constant. The experimental K_p data represent the combined contribution of both components to the isotherms. The interpretation of the binary K_p data has been treated by several methods (Van der Vlist and Van der Meijden, 1973; Buffman et al., 1985, 1999; Triebe and Tezel, 1995; Kabir et al., 1998).

The method of Kabir *et al.* (1998) is based on determining the activity coefficients from the binary retention time data. For ideal mixtures, these values are related to Ideal Adsorbed Solution Theory suggested by Myers and Prausnitz (1965). For the case of non-ideal mixtures, the use of the Regular Solution Model (Siperstein et al., 1997) was used. Both of these approaches allow for the determination of binary adsorption isotherms. However, the extent of their applicability is related to the degree of the fit of the binary K_p data. Further, experimental data up to pressures allowing for the applicability of the IAST are also required.

For the method of Buffman *et al.* (1985), a retention time is related to each of the flowrate and concentration transients at the outlet. These transients are then related to the phase behavior of the mixture. From this information, the slopes of the isotherms are found. This method was furthered by Mason and Buffman (1996) to include the effects of pressure changes.

Another approach was developed by Buffman *et al.* (1999). In the method a form of the binary isotherms is assumed and the corresponding K_p function is determined. Although Buffman *et al.* used the binary Langmuir isotherm for illustration purposes; any binary isotherm model can be used. With this approach, a well-established isotherm model is applied, however, not all binary adsorption systems may follow the chosen model. This can be seen by the quality of the experimental binary K_p data regression.

The procedure for evaluating binary isotherms is generally performed by fitting the K_p vs. mole fraction (y_1) data to a function of i parameters that can fit the data well:

$$K_p(\text{Experimental}) = \boldsymbol{f}(A_i, y_1) \tag{5}$$

Following this functional form, the isotherm slope functions are defined with unknown parameters, B_j

and C_j, as follows.

$$\frac{dq_1}{dP_1} = \frac{d\boldsymbol{f}(A_i, y_1)}{dy_1} = \mathbf{g}(B_j, y_1) \tag{6}$$

$$\frac{dq_2}{dP_2} = \frac{d\boldsymbol{f}(A_i, y_1)}{dy_1} = \mathbf{h}(C_j, y_1) \tag{7}$$

The A_i parameters are determined by non-linear regression of the experimental K_p vs. y_1 data. The B_j and C_j parameters can be determined by initially substituting component 1 and 2 isotherm slope expressions (Eqs. (6) and (7)), into Eq. (3). This expression is then set equal to the regressed form of Eq. (5), as follows:

$$K_\mathrm{p} = \boldsymbol{f}(A_i, y_1) = (1 - y_1)[\boldsymbol{g}(B_j, y_1)] + y_1[\boldsymbol{h}(C_j, y_1)] \tag{8}$$

Since the A_i parameters are known through regression, factoring like terms reveals ***i*** identities and a system of equations is developed.

Two other equations must be added to the system in order to solve for the unknowns. These equations come from the pure component isotherm end-points:

$$q_1(\mathrm{pure})|_{P_\mathrm{Total}} = q_1(\mathrm{binary})|_{y_1=1} = P_\mathrm{Total} \int_0^{y_1} \boldsymbol{g}(B_j, y_1)\, dy_1 \tag{9}$$

$$q_2(\mathrm{pure})|_{P_\mathrm{Total}} = q_2(\mathrm{binary})|_{y_1=0} = P_\mathrm{Total} \int_1^{y_1} \boldsymbol{h}(C_j, y_1)\, dy_1 \tag{10}$$

The solution determines the B_j and C_j parameters, which are used in the integrated forms of Eqs. (6) and (7) to determine the binary isotherms, q_1 and q_2 as functions of y_1.

Two different functional forms of Eq. (5) have been suggested in the literature to determine the binary isotherms. The most often used form is the 3rd degree polynomial, (Van der Vlist and Van der Meijden, 1973; Ruthven and Kumar, 1980; Heslop et al., 1996; Tezel et al., 1992):

$$K_\mathrm{p} = A_0 + A_1 y_1 + A_2 y_1^2 + A_3 y_1^3 \tag{11}$$

where the isotherm slopes are given by Eqs. (12) and (13).

$$\frac{dq_1}{dP_1} = B_0 + B_1 y_1 + B_2 y_1^2 \tag{12}$$

$$\frac{dq_2}{dP_2} = C_0 + C_1 y_1 + C_2 y_1^2 \tag{13}$$

The isotherm equations are found by the integration of Eqs. (12) and (13).

$$q_1 = \left(B_0 y_1 + \frac{B_1}{2} y_1^2 + \frac{B_2}{3} y_1^3\right) P_\mathrm{Total} \tag{14}$$

$$q_2 = \left[C_0(1 - y_1) + \frac{C_1}{2}(1 - y_1^2) + \frac{C_2}{3}(1 - y_1^3)\right] P_\mathrm{Total} \tag{15}$$

Substituting Eqs. (11), (12), and (13) into Eq. (8) results with Eq. (16):

$$\begin{aligned} A_0 + A_1 y_1 + A_2 y_1^2 + A_3 y_1^3 &= \big[(1 - y_1)\big(B_0 + B_1 y_1 + B_2 y_1^2\big) \\ &\quad + y_1\big(C_0 + C_1 y_1 + C_2 y_1^2\big)\big] \end{aligned} \tag{16}$$

In order to solve for the B_j and C_j parameters, the following system of equations is developed by equating the coefficients of similar terms in Eq. (16).

$$A_0 = B_0 \tag{17}$$

$$A_1 = C_0 - B_0 + B_1 \tag{18}$$

$$A_2 = C_1 - B_1 + B_2 \tag{19}$$

$$A_3 = C_2 - B_2 \tag{20}$$

By using the pure component end points, the final two equations needed to solve the system are developed:

$$q_1(\mathrm{Pure})|_{P_\mathrm{Total}} = P_\mathrm{Total}\left(B_0 y_1 - \frac{B_1}{2} y_1^2 + \frac{B_2}{3} y_1^3\right)\Bigg|_{y_1=1} \tag{21}$$

$$\begin{aligned} q_2(\mathrm{Pure})|_{P_\mathrm{Total}} = P_\mathrm{Total}\Bigg(&C_0(1 - y_1) \\ &+ \frac{C_1}{2}(1 - y_1^2) + \frac{C_2}{3}(1 - y_1^3)\Bigg)\Bigg|_{y_1=0} \end{aligned} \tag{22}$$

This system of equations is solved and the B_j and C_j parameters are determined. These values then determine the binary isotherms, as given by Eqs. (14) and (15).

For the purposes of this work, the method of Van der Vlist and Van der Meijden will be termed VV-CPM (Van der Vlist and Van der Meijden—Concentration Pulse Method).

Hyun and Danner (1982) and Heslop *et al.* (1996) critically reviewed this method. Hyun and Danner

(1982) found that the VV-CPM will result with binary isotherms that coincide with binary isotherms directly measured by volumetric methods if the polynomial fit was well representing the experimental K_p data. When the use of the polynomial function for describing the experimental binary K_p data was not accurate, the validity of this method was in question.

Heslop *et al.* (1996) also examined the validity of the VV-CPM and came to the same conclusion as Hyun and Danner (1982). They also examined the applicability when the polynomial was assumed to be 4th order instead of the common 3rd order. With the 4th order expression, more system dependent information was required in order to solve the system of equations that resulted. To alleviate this problem, they assumed a value of the amount adsorbed for component A and added the result to the system of equations in order to balance the degrees of freedom. They claimed that the 4th order polynomial could represent the binary system more accurately than the 3rd order. However, since this type of extra information needed for the 4th order polynomial is not usually available, the validity of this modification is questionable. They further examined the effect of the objective function for determining the optimal parameters in the regression. They determined that the objective function had little effect on the quality of the fit. However, in their results, the binary K_p data did not vary drastically, and therefore, the effect of data point bias was minimal.

Another function for describing the binary K_p data was developed by Triebe and Tezel (1995). The following 5-parameter function was used:

$$K_p = A_{-1}(\beta + y_1) + A_0 + \frac{A_1}{(\beta + y_1)} + \frac{A_2}{(\beta + y_1)^2} \tag{23}$$

where the isotherm slopes are given by Eqs. (24) and (25):

$$\frac{dq_1}{dp_1} = B_0 + \frac{B_1}{(\beta + y_1)} + \frac{B_2}{(\beta + y_1)^2} \tag{24}$$

$$\frac{dq_2}{dp_2} = C_0 + \frac{C_1}{(\beta + y_1)} + \frac{C_2}{(\beta + y_1)^2} \tag{25}$$

The β term appearing in Eqs. (24) and (25) is the same β value found by the non-linear regression of Eq. (23) to the experimental binary K_p data.

The isotherm equations are found by integrating Eqs. (24) and (25) and are given as follows:

$$q_1 = P_{\text{Total}}\left[B_0 y_1 + B_1 \ln\left\{\frac{(\beta + y_1)}{\beta}\right\} + \frac{B_2 y_1}{\beta(\beta + y_1)}\right] \tag{26}$$

$$q_2 = P_{\text{Total}}\left[C_0(1 - y_1) - C_1 \ln\left\{\frac{(\beta + y_1)}{(\beta + 1)}\right\} + \frac{C_2(1 - y_1)}{(\beta + 1)(\beta + y_1)}\right] \tag{27}$$

Substituting Eqs. (23)–(25) into Eq. (8) and equating the coefficients of the similar terms yields the following system of equations to be solved for the determination of B_j and C_j parameters:

$$A_{-1} = C_0 - B_0 \tag{28}$$

$$A_0 = B_0(\beta + 1) - B_1 - C_0\beta + C_1 \tag{29}$$

$$A_1 = B_1(\beta + 1) - B_2 - C_1\beta + C_2 \tag{30}$$

$$A_2 = B_2(\beta + 1) - C_2\beta \tag{31}$$

$$q_1(\text{Pure})|_{P_{\text{Total}}} = P_{\text{Total}}\left(B_0 y_1 + B_1 \ln\left\{\frac{(\beta + y_1)}{\beta}\right\} + \frac{B_2 y_1}{\beta(\beta + y_1)}\right)\Bigg|_{y_1=1} \tag{32}$$

$$q_2(\text{Pure})|_{P_{\text{Total}}} = P_{\text{Total}}\left(C_0(1 - y_1) - C_1 \ln\left\{\frac{(\beta + y_1)}{(\beta + 1)}\right\} + \frac{C_2(1 - y_1)}{(\beta + 1)(\beta + y_1)}\right)\Bigg|_{y_1=0} \tag{33}$$

For the purposes of this work, the method of Triebe and Tezel will be termed TT-CPM (Triebe and Tezel—Concentration Pulse Method).

There are similarities between using the polynomial function (VV-CPM) and using the function suggested by Triebe and Tezel (1995), (TT-CPM), for the development of the system of equations. First, the number of parameters that can be used in Eq. (5) is limited to limited to 4. This is due to the restriction from the number of equations that can be developed from the use of Eq. (8) and the number of equations required to exhibit a unique solution. For a binary system the following relationship is derived.

$$\begin{aligned} \text{Number of Unknown Parameters} &= 2j \\ \text{Number of Equations Possible} &= i + 2 \end{aligned} \tag{34}$$

Table 1. Equation-unknown combinations for use with the Van der Vlist-Van der Meijden method.

Indices		Number of equations	Number of unknowns	Degrees	
i (Eq. 5)	j (Eqs. 6 and 7)	$(i+2)^a$	$(2j)$	of freedom	Result
1	0	3	0	3	Over-specified
2	1	4	2	2	Over-specified
3	2	5	4	1	Over-specified
4	3	6	6	0	Satisfied
5	4	7	8	−1	Under-specified
6	5	8	10	−2	Under-specified
7	6	9	12	−3	Under-specified

[a] The 2 results from the use of the pure component isotherm end points ($y_1 = 0, 1$).

where i is the number of parameters in Eq. (5) and j is the number of B and C parameters in Eqs. (6) and (7). For this relationship, the isotherm end-points are always included as equations. This ensures that the binary isotherms adhere to the pure isotherms at the end-points. The possible solutions to Eq. (34) are shown in Table 1. It shows that for $i < 4$ the system is over specified and therefore a number of solutions will exist. When $i > 4$, the system is under specified and additional data is required in order to obtain a unique solution. However, this data is usually not available. Therefore, the number of parameters that can be used in Eq. (5) to provide a unique solution is where $i = 4$ and thus $j = 3$.

Since the objective is to fit the data as well as possible, different functions and/or more parameters could be used. However, if a different function is used it must conform to the constraints of Eq. (8); the chosen function, $f(A_i, y_1)$ and the right hand side of Eq. (8) must contain like terms for a system of equations to be developed. This fact limits the functional form that can be used in Eq. (5) and the number of parameters that it contains.

The Novel Approach

When the literature was reviewed on the concentration pulse method (CPM), it was observed that previous methods based on the VV-CPM introduced false system behavior for some binary systems where K_p changes drastically between $y_1 = 0$ and $y_1 = 1$. This false behavior comes from the characteristic oscillations inherent to the use of the polynomial function and results in negative K_p values. Therefore, the objective of this work was to eliminate these behaviors. However, due to the constraints of the methods (VV-CPM and TT-CPM), this objective can only be obtained by modifying the solution procedure for determining the B_j and C_j parameters. This was accomplished by first using any functional form for the regression of the experimental K_p data and by noting that the K_p values defined by Eq. (5), and Eq. (8), should be approximating the same K_p values found experimentally. Therefore, in order to solve for the unknown B_j and C_j parameters, the right-hand side of Eq. (8) can be equated to the experimental data points.

$$K_p(\text{Experimental}) = (1 - y_1)[\boldsymbol{g}(B_j, y_1)] + y_1[\boldsymbol{h}(C_j, y_1)] \qquad (35)$$

In order to regress the experimental data, an objective function must be established. For this solution procedure, the objective function was defined to minimize the sum of residuals of Eq. (35), with respect to the experimental K_p data.

$$(\text{Sum Of Residuals})^2 = \sum_{y=y_{\min}}^{y=y_{\max}} (K_p[\text{Experimental}] - K_p[\text{RHS \{Eq. (35)\}}])^2 \qquad (36)$$

The properties of the adsorbent and adsorbates must also be considered in the solution. As discussed by Calleja *et al.* (1998), an overadsorption effect (*non-ideality*) can be seen with polar-nonpolar adsorbates with a more homogeneous adsorbent (*high* SiO_2/Al_2O_3 *ratios*). This interaction of adsorbate-adsorbate-adsorbent, especially at high loading levels could cause a nonideal behavior of the mixture and results in an azeotrope. If this occurs, a maximum in the binary adsorption isotherm could occur. However, at the loading levels of the present study, for adsorbates that are similar in properties (*such as the* CO_2 *and* N_2 *system*), overadsorption could not occur. Therefore, no maximum in the adsorption isotherm should appear.

The minimization of Eq. (36) should not be performed with only the data, since a number of solutions will exist. The following constraints are imposed on the system (*including the facts mentioned in the previous paragraph*) as a basis for the method, in order to ensure that the solution reflects what is physically occurring.

1) The end-points of the binary isotherms must coincide with the pure isotherms:

$$q_1(\text{Binary})|_{y_1=1} = q_1(\text{Pure})|_{P_{\text{Total}}} \tag{37}$$

$$q_2(\text{Binary})|_{y_1=0} = q_2(\text{Pure})|_{P_{\text{Total}}} \tag{38}$$

2) If the adsorbates are similar in properties and adsorption occurs at low fractional loading, θ, the isotherm slopes must be greater than or equal to zero across the entire range of y_1 (*i.e. no maximum should be seen in the isotherms*):

$$\frac{dq_1}{dy_1} \geq 0 \quad \text{and} \quad \frac{dq_2}{dy_2} \geq 0 \tag{39}$$

3) The K_p function should pass through the experimental binary K_p data at $y_1 = 0$ and $y_1 = y_1$ (max):

$$K_p(\text{experimental})|_{y_1=0} = K_p(\text{Eq. 5})|_{y_1=0} \tag{40}$$

$$K_p(\text{experimental})|_{y_1\to 1} = K_p(\text{Eq. 5})|_{y_1\to 1} \tag{41}$$

The constraint given by Eq. (40) is used to ensure that the regressed curve does not predict a higher initial slope than what was obtained experimentally. The constraint given by Eq. (41) is used to ensure that the regressed K_p curve does not violate the physical bounds of the system and produce negative values.

By using these constraints (Eqs. (37)–(41)) to bind the objective function, Eq. (36), the unknown B_j and C_j parameters can be determined. These regressed parameters are then used in appropriate integrated forms of Eqs. (6) and (7) for the calculation of the binary isotherms.

For this study the functional forms given by Eqs. (23)–(25) were used. The isotherms are given by Eqs. (26) and (27). The regressed K_p function is given by the appropriate substitutions (Eqs. (24) and (25)) into Eq. (35) and is given as follows:

$$\begin{aligned} &K_p(\text{Experimental}) \\ &\quad = (1-y_1)\left[B_0 + \frac{B_1}{(\beta+y_1)} + \frac{B_2}{(\beta+y_1)^2}\right] \\ &\qquad + y_1\left[C_0 + \frac{C_1}{(\beta+y_1)} + \frac{C_2}{(\beta+y_1)^2}\right] \end{aligned} \tag{42}$$

The objective function is given by:

$$\begin{aligned} SSR = \sum_{y_1=y_{\min}}^{y_1=y_{\max}} \{&K_p[\text{Experimental}] \\ &- K_p[\text{RHS}\{\text{Eq. (42)}\}]\}^2 \end{aligned} \tag{43}$$

subject to the constraints given by Eqs. (37)–(41).

For the purposes of this work, this novel solution procedure will be termed MTT-CPM (Modified Triebe and Tezel—Concentration Pulse Method).

Objective

The purpose of this study was to compare the use of the two methods previously described in the literature with the novel solution procedure proposed in this work for the determination of the B_j and C_j parameters. The adsorption system studied was CO_2-N_2 on H-ZSM-5-30 and H-ZSM-5-280. The values 30 and 280 for these adsorbents represent the SiO_2/Al_2O_3 ratios of 30 and 280. This variation with the SiO_2/Al_2O_3 ratio allowed for the degree of surface interaction of the adsorbent with the adsorbates to be observed. The H-ZSM-5-30 has a more heterogeneous surface than H-ZSM-5-280, as more alumina in the structure results in more cations to obtain structural neutrality to make-up for the charge difference between Si^{+4} and Al^{+3}.

The data obtained with the suggested solution procedure, MTT-CPM, is compared to the results obtained using the solution procedures of VV-CPM and TT-CPM. Binary isotherms, *x-y* adsorption phase diagrams and separation factor plots are given for the system of gases studied: CO_2-N_2 mixtures on H-ZSM-5 with SiO_2/Al_2O_3 ratios equal to 30 and 280.

Experimental

A schematic diagram of the experimental apparatus is shown in Fig. 1. The details of the gases used are given

Table 2. Gases used in pure and binary adsorption runs.

Type	Grade	Purity	Supplier
He	Ultra pure carrier	99.998%	Air Products
CO_2	Research	99.995%	Air Products
N_2	Ultra high purity	99.999%	Air Products

Table 3. Experimental and column specifications.

ZSM-5 pore diameter	6.0	Å
Particle size	20–60	Mesh
Average particle diameter	545	μm
% Binder (wt)	16.5	
Binder type	KAOLIN	
Bed porosity	0.382	
Column length	24.75	cm
Column inner diameter	0.45	cm
Total flowrate	40.0	cc/min@40°C
Total pressure	1.0	Atm.
Column adsorption temperature	40.0	°C
Regeneration temperature	350	°C
Regeneration pressure	1.0	Atm.
Regeneration time	12	Hours

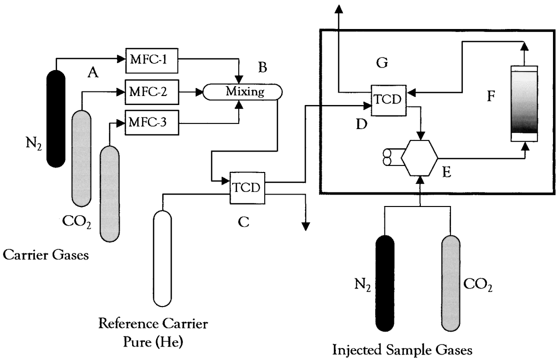


Figure 1. Schematic diagram of the experimental setup. (A)-Carrier gases and MFC's. (B)-Mixing chamber. (C)-Carrier gas TCD. (D)-Reference side of column TCD. (E)-Injection valve. (F)-Packed column within GC oven. (G)-Sample side of column TCD.

in Table 2. The experimental and column characteristics are given in Table 3.

As shown in Fig. 1, the flowrates and mixing of the gases (A) were controlled by a series of MKS mass flow controllers (MFC), model number 1359 (0–50 sccm range), and set to a total flowrate of 40 cc/min at 40°C. A mixing chamber (B) was installed after the MFC's to ensure a homogeneous mixture in the carrier gas. A thermal conductivity detector (TCD) with a GOW-MAC power supply (C) was placed after the mixing chamber to measure the composition of the carrier gas and thus ensure mixture stability. The carrier gas was then passed through the reference side of the TCD in the GC (D). This TCD was used to measure the response of the column to the sample injection (E). After the injection, the carrier and sample passed through the packed column (F) and the response was measured (G).

Data acquisition was performed using a National Instruments based data acquisition card and Labview v5.0 on an Intel based computer. Each column was independently packed with H-ZSM-5 adsorbents and was contained within a Varian 3400 gas chromatograph at 40°C. The GC was equipped with a high sensitivity thermal conductivity detector.

Before the start of each experimental run, the adsorbent was regenerated at 1.0 atmosphere total pressure and 350°C under a 40 cc/min (at 40°C) helium purge, for approximately 12 hours.

In order to determine the system dead time, a helium injection into the nitrogen carrier was used. The regenerated adsorbent packed column was then allowed to reach equilibrium with the N_2 carrier. The equilibrium state was confirmed by noting the response of the detector. The TCD operates on a wheat-stone bridge principle. Therefore, a steady baseline would indicate that the composition and flowrate of the influent was equal to the effluent. Next, an injection of He was made. Helium gas was used since it is non-adsorbing. This property allows for an accurate measure of the time required for the pulse to travel through the void space of the tubing and the adsorbent packed column.

In order to determine pure gas isotherms, helium (He) was mixed with the adsorbate and used as the carrier gas. The concentration of the adsorbate was incrementally increased from zero to approximately 98% in the carrier. Equilibrium of the gas mixture with the adsorbent after a change in carrier gas composition was assured by examining the recorder trace for complete breakthrough of the influent mixture. After equilibrium was reached, a sample pulse of adsorbate (0.25 cc) was injected into the column, and the response at the column outlet was recorded. The injection was repeated several times over several hours. This enabled the verification of equilibrium, as the measured K_p value did not change except within the experimental error. This was repeated for different adsorbate concentrations in the carrier gas.

Table 4. Adsorbate properties.[a]

	Property				
Adsorbate	Molecular weight	Kinetic radius (Å)	Dipole moment × 10^{18} (esu cm)	Quadrupole moment × 10^{26} (esu cm^2)	Polarizability × 10^{25} (cm^3)
CO_2	44	3.30	0	4.30	26.5
N_2	28	3.64	0	1.52	17.6

[a] Golden and Sircar (1994).

When determining binary isotherms, mixed carriers were used without the He gas. For the CO_2-N_2 system, N_2 was used as the primary gas. Samples of each gas were injected into the column at different carrier gas concentrations.

It is important to note that the experimental data represents binary isotherm's effective slope at a particular mixture composition. As the injection volume approaches zero (for this study, a 0.25 cc sample loop was used), the K_p values found by both injections should be indentical. When CO_2 is injected, the mixture composition increases slightly in CO_2 concentration. When N_2 is injected, the mixture composition decreases slightly in CO_2 concentration. Therefore, both adsorbates are injected into the mixed carrier gas and the arithmetic average K_p value was found. During this study, the mean retention times found for CO_2 and N_2 during the binary study did not vary by more than 5%.

Adsorbents-Adsorbates

The adsorbents used in this study were H-ZSM-5 with silica to alumina (SiO_2/Al_2O_3) ratios of 30 and 280. They were prepared and donated by Dr. Ahmet Sirkecioglu, of the Department of Chemical Engineering at Istanbul Technical University in Istanbul, Turkey. They were supplied in powder form, which is not appropriate for use with the CPM, since a large pressure drop and possible adsorbent loss due to flow would be encountered. Therefore, the adsorbent powder was combined with a Kaolin binder. A 16.5 wt% binder was used in order to maintain sufficiently high enough pellet strength when exposed to the conditions of the experiments. The pellets, which are composed of binder and adsorbent, were sized to 20–60 mesh. All the results given in this work are corrected with respect to the 16.5 wt% binder and therefore represent properties of the pure ZSM-5 without the binder.

The H-ZSM-5 adsorbent is a pentasil zeolite with the silicalite structure. The crystalline structure consists of eight double 5-member rings built around two double 6-member rings forming a double 10-membered ring unit cell. These 10-membered rings combine to form the lattice structure, which in turn combine to form the crystalline structure (Yamazaki et al., 1993).

The adsorbates examined in this study were CO_2 and N_2. A summary of some of the properties of these adsorbates is given in Table 4.

Numerical Methods

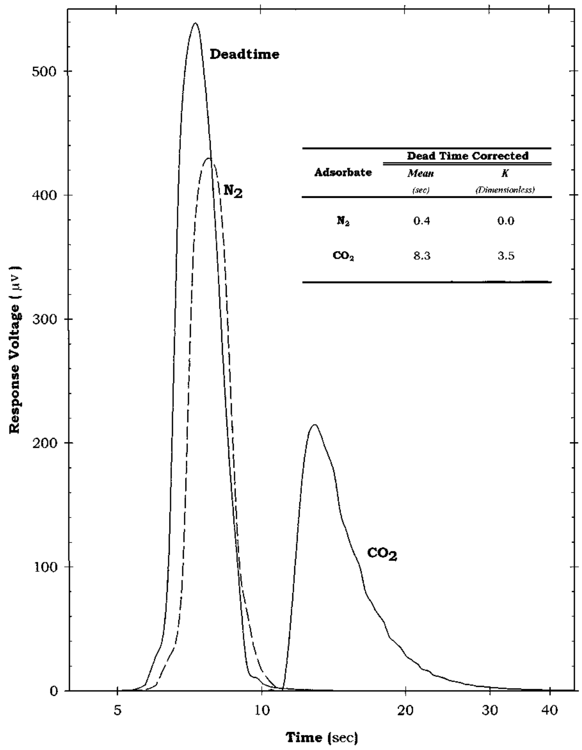
A non-linear regression was performed using a modified Levenberg-Marquardt algorithm with a finite difference Jacobian in order to determine the parameters for the pure component isotherm fits to the Toth isotherm as well as the K_p regressions for Eqs. (11) and (23).

In order to solve the system of equations given by the TT-CPM (Eqs. (28)–(33)) a non-linear equation solver was used. This method was based on Newton's method and employed a finite-difference approximation to the Jacobian (Dennis et al., 1983). In order to determine the optimal values of the B_j and C_j parameters for the MTT-CPM a non-linear constrained optimization technique was used (Gill et al., 1981, 1985). This was based on a Generalized Reduced Gradient (GRG2) nonlinear optimization code. Quadratic extrapolation was employed to obtain initial estimates of the basic variables in each one-dimensional search (Powell 1977, 1978). The Jacobian for the objective and constraint functions were approximated by a central finite difference approach (Dennis et al., 1983). A quasi-Newton iteration method was also used. Tolerance and convergence were each set at 10^{-6}. The solution was taken when no further change in the objective function (Eq. (43)) could be obtained for a wide range of starting values. This wide range of initial guesses ensured that the absolute and not the local minimum was obtained.

Results

Kaolin Binder

The Kaolin binder was tested for adsorption characteristics at 0% loading with CO_2 and N_2, at the conditions used in this study. Pure Kaolin was pelletized into 20–60 mesh and was packed into the adsorption column. It was then regenerated at 350°C for 12 hours under a 40 cc/min (at 40°C) He purge. Injections of each of the adsorbates studied were then performed and the column response was noted. The results are shown in Fig. 2. The dead time response of the system is also shown, with respect to the Kaolin packed column. The data shown in Fig. 2 confirms that the contribution of the binder to the adsorption characteristics is negligible for N_2. The binder does have a small effect on the adsorption characteristics of CO_2. However, magnitude of this contribution is negligible in comparison to the values obtained with the adsorbent + binder. Further, the contribution of the binder will decrease as the carrier gas composition of each of the adsorbates is increased. Therefore, the Kaolin binder is considered as inert filler, under the conditions used in this study. All the results obtained are corrected according to the 16.5 wt% binder in the adsorbent, so that the results given reflect the properties of the pure H-ZSM-5.



Adsorbate	Dead Time Corrected	
	Mean *(sec)*	*K* *(Dimensionless)*
N_2	0.4	0.0
CO_2	8.3	3.5

Figure 2. Column response for the determination of dead time and the effect of pure kaolin binder for different adsorbates.

Pure Isotherms

Pure gas isotherms with both adsorbents for CO_2 and N_2 at 40°C are shown in Figs. 3 and 4 respectively. The amount adsorbed is represented on a binder free basis. The pure isotherms were determined by first regenerating the adsorbent, then going through an adsorption run, then purge desorption run, then adsorption run again for various compositions of y_1. The desorption was performed by lowering the CO_2 or N_2 mole fraction in He from 100% down to 0% and injecting samples after attaining equilibrium after each concentration change. Equilibrium of the mixture with the adsorbent was confirmed by noting that the change in the K_p values at a given y_1 composition would converge as equilibrium was approached. When equilibrium was reached, a final series of injections were given, and arithmetic average K_p value was determined, and the concentration of CO_2 or N_2 was lowered again. The results of this series of runs are shown in Figs. 3 and 4 for pure component CO_2 and N_2, respectively. Volumetric data previously obtained in our laboratories for the same system are also shown in these figures for comparison. As can be seen from these figures, isotherms obtained by CPM matches the volumetric data very well.

All the experimental data obtained with the concentration pulse method (CPM) were combined and fit to the Toth isotherm according to Eq. (44), (Do, 1998):

$$q = \frac{q_m bP}{[1 + (bP)^n]^{1/n}} \tag{44}$$

and shown as best fit curves in Figs. 3 and 4.

The CO_2 adsorption capacity with H-ZSM-5-30 is almost double the capacity with H-ZSM-5-280. This suggests that CO_2 adsorption capacity is higher for H-ZSM-5 if surface is more heterogeneous with more cations in the structure (*because of more* Al^{+3}). These results are in agreement with the results obtained in the literature by Calleja *et al.* (1998). They studied the adsorption of pure CO_2 with ZSM-5 zeolites with different SiO_2/Al_2O_3 ratios and found that as this ratio decreased, CO_2 adsorption capacity increased.

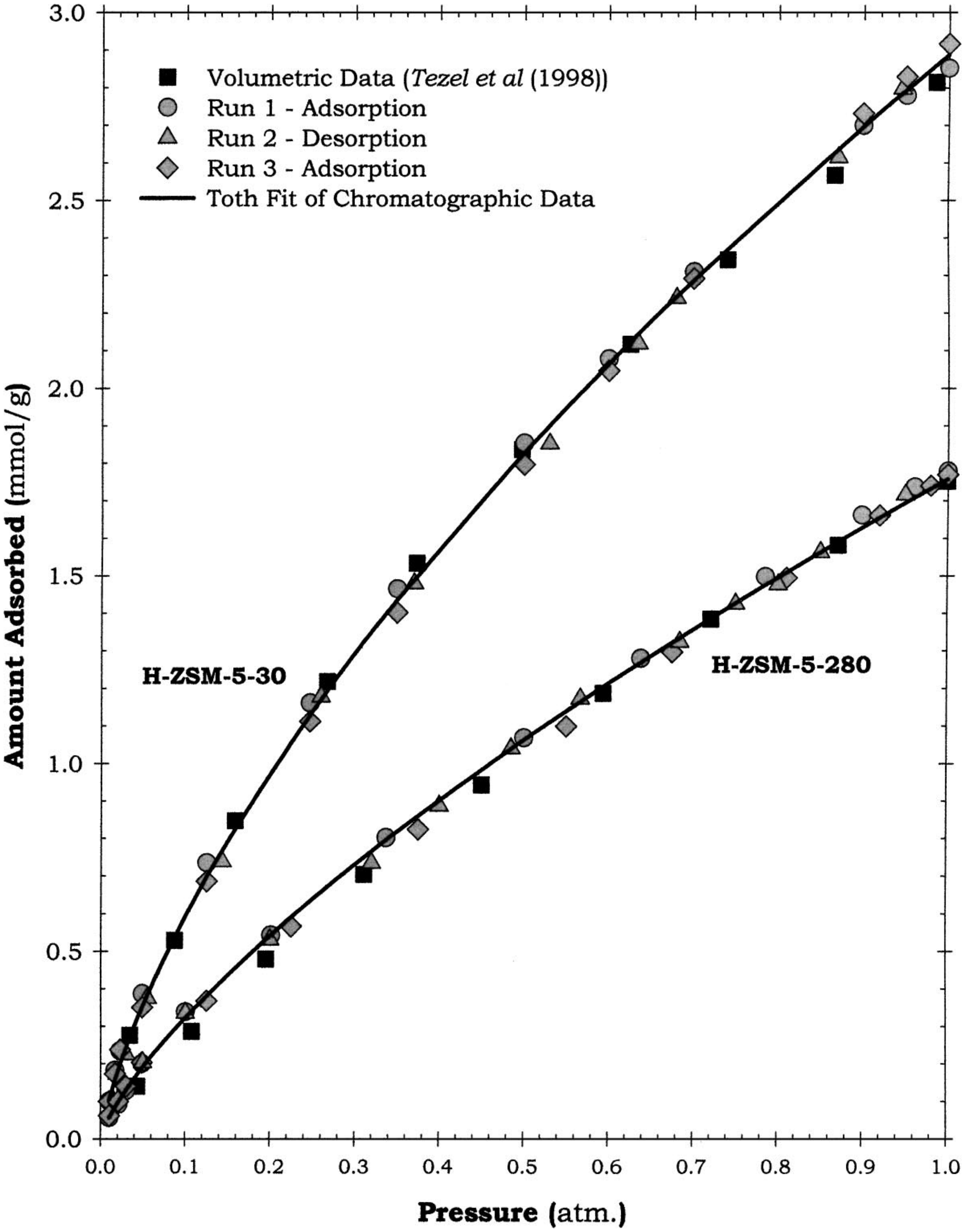


Figure 3. Pure component CO_2 isotherms determined chromatographically for H-ZSM-5-30 and H-ZSM-5-280 at 40°C. Volumetric data from Tezel *et al.* (1998).

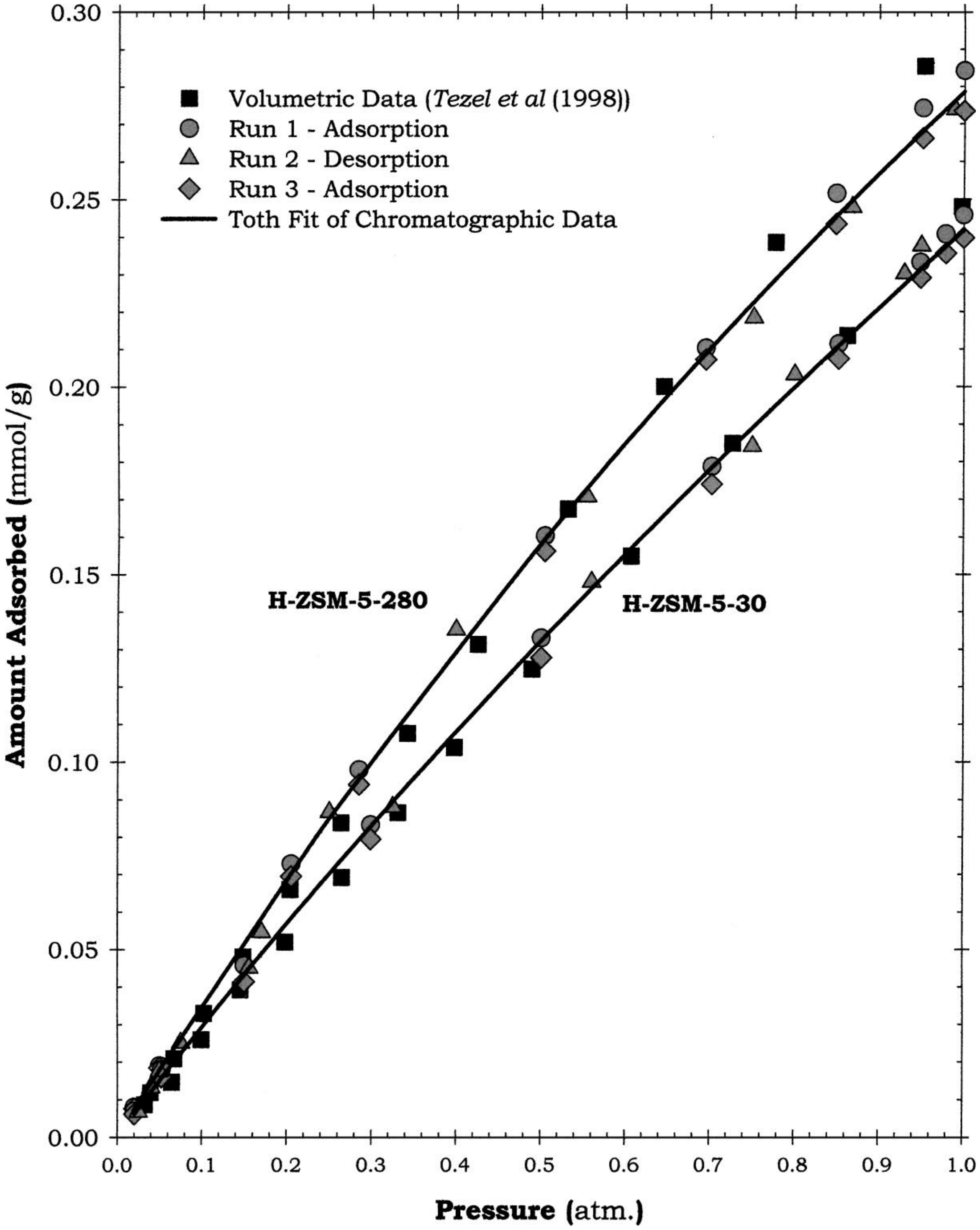


Figure 4. Pure component N_2 isotherms determined chromatographically for H-ZSM-5-30 and H-ZSM-5-280 at 40°C. Volumetric data from Tezel *et al*. (1998).

Figure 4 shows that for the adsorption of N_2, the order was reversed. H-ZSM-5-280, which had a higher SiO_2/Al_2O_3 ratio with a less degree of heterogeneity, had a higher capacity for N_2 (Saito and Foley, 1995). This trend in adsorption capacities for N_2 and CO_2 is very promising for ZSM-5 as an adsorbent for applications in CO_2 removal from air.

Reversibility of the pure component adsorption isotherms confirms that physical adsorption occurs for both CO_2 and N_2 with H-ZSM-5 with no hysteresis effects.

Binary Isotherms

The results of the binary study with the VV-CPM (*the polynomial function according to Eq. (11)*) did not result with a regression curve that could resemble the experimental K_p data at all, since it introduced oscillations that does not represent the data obtained. From this result, it was concluded that the VV-CPM would not result with any meaningful data for the systems studied. Further, it was observed that this was the case for all the systems where there was a large difference in the adsorption capacities of the two components in the binary system. Therefore, the VV-CPM should not be used to describe these systems.

The experimental binary K_p data for the CO_2-N_2 systems and the TT-CPM regressions are shown in Fig. 5 for H-ZSM-5-30 and H-ZSM-5-280. The TT-CPM regressed function (Eq. (23)), appears to fit the experimental data across the entire range of y_1. However, upon closer examination of the fit provided by Eq. (23) for H-ZSM-5-30, the regressed values go negative as the mole fraction of CO_2 approaches 0.90, which is physically meaningless for adsorption.

In order to define the TT-CPM binary isotherms, the B_j and C_j parameters were determined from the solution of Eqs. (28)–(33). The resulting binary isotherms are given in Fig. 6 for H-ZSM-5-30 and Fig. 7 for H-ZSM-5-280. By using the TT-CPM, the binary isotherms obtained are not feasible. N_2 isotherms for both H-ZSM-5-30 and H-ZSM-5-280 violate the physical nature of the system by giving negative values for the amount adsorbed. This behavior may be due to the functional form used for regressing the experimental K_p data, which was predicting negative K_p values (Fig. 5). This demonstrates the importance of the regression of the experimental data. It was concluded that the TT-CPM should not be used for systems where there are relatively large differences in the pure component adsorption capacities.

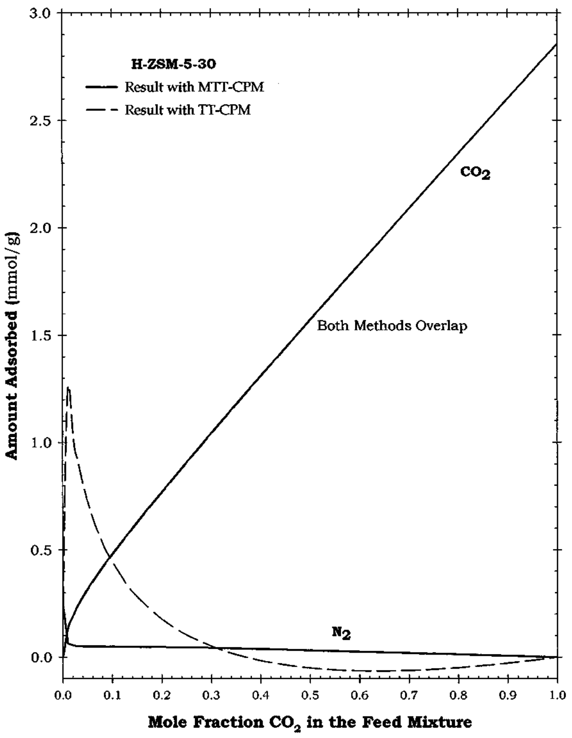


Figure 6. Binary CO_2-N_2 isotherms with H-ZSM-5-30 at 1.0 atm. total pressure and 40°C, obtained using TT-CPM and MTT-CPM techniques.

Proposed Method

The CO_2-N_2 binary isotherms obtained with the proposed solution method (MTT-CPM) for H-ZSM-5-30 and H-ZSM-5-280 are also given in Figs. 6 and 7, respectively. The B_j and C_j parameters were determined directly from the regression of the experimental K_p data with the use of the objective function and the constraints given by Eqs. (37)–(41). The CO_2 binary isotherm is not greatly affected by the solution method. This is due to the relative adsorption capacities of the two components; the N_2 isotherm is much lower than the CO_2 isotherm for both adsorbents. Therefore, a binary adsorption system of these types could be construed as stiff systems, and thus cause the relationships observed with the TT-CPM. However, the effect of constraining the regression to the form proposed with the MTT-CPM causes the N_2 binary adsorption isotherm to exhibit behavior that does not violate the physical nature of the system.

The binary isotherms obtained with the MTT-CPM for both adsorbents studied are also given in Fig. 8.

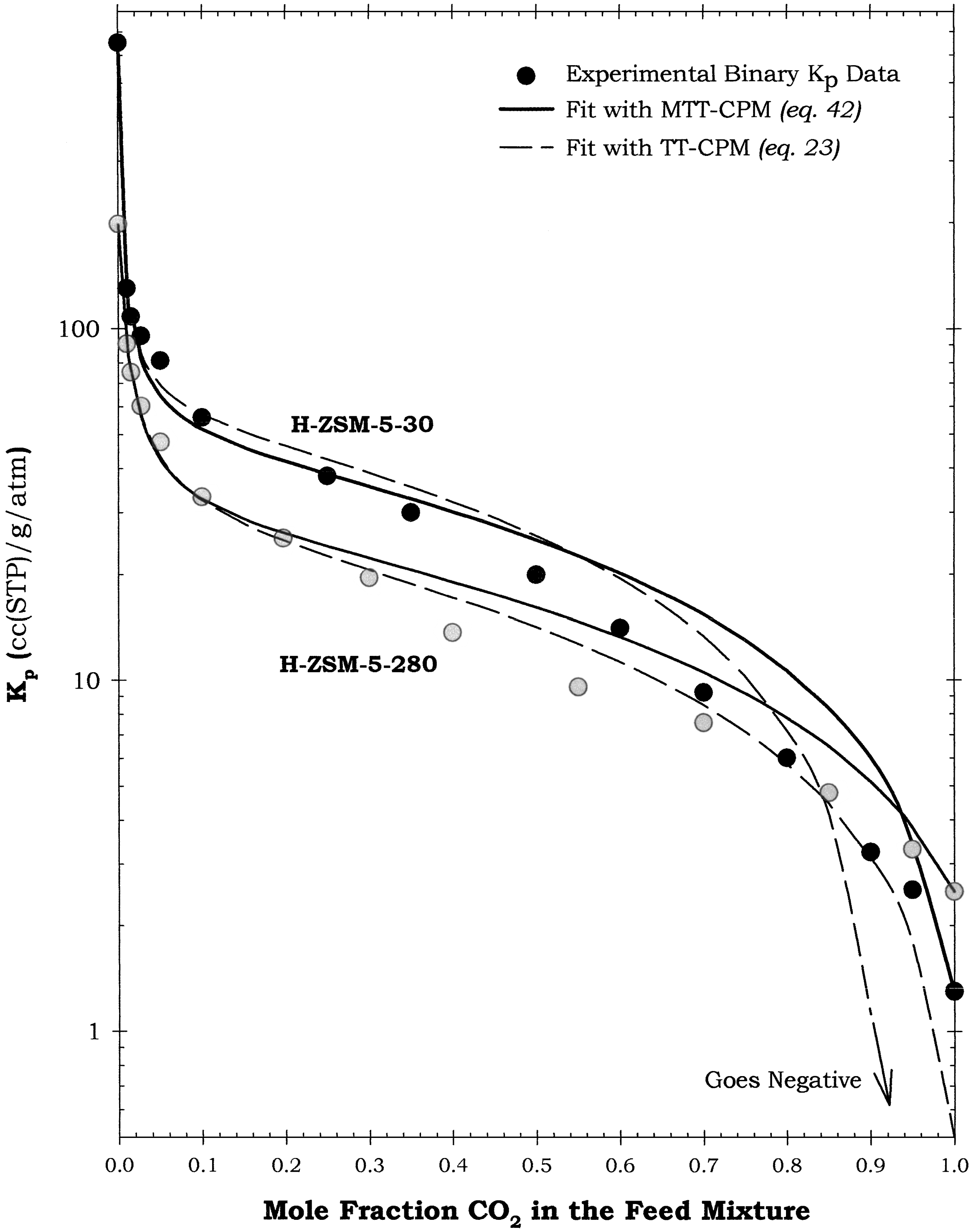


Figure 5. Experimental CO_2-N_2 binary K_p data for H-ZSM-5-30 and H-ZSM-5-280 at 40°C and 1.0 atmosphere total pressure, compared with regressions for Eqs. (23) and (42).

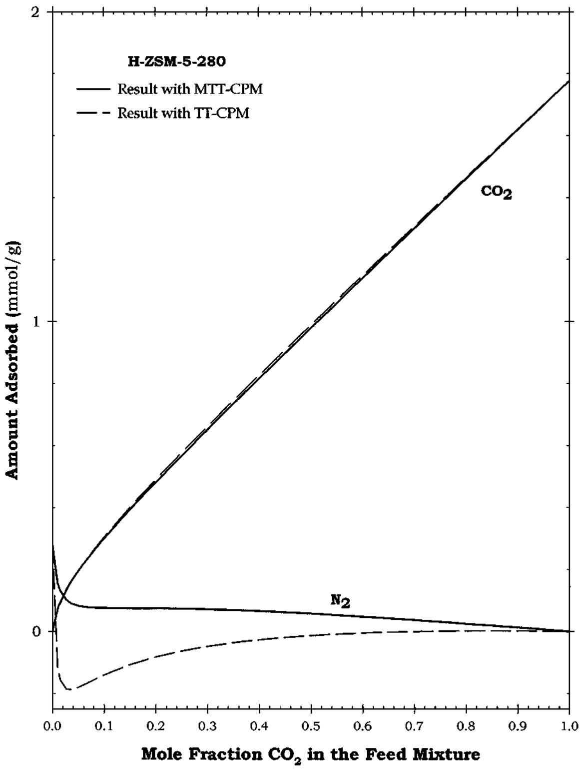


Figure 7. Binary CO_2-N_2 isotherms with H-ZSM-5-280 at 1.0 atm. total pressure and 40°C, obtained using TT-CPM and MTT-CPM techniques.

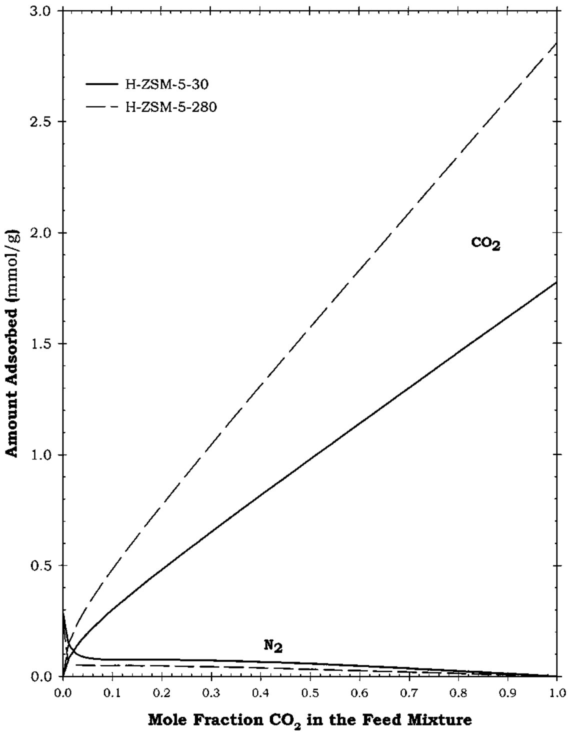


Figure 8. Binary CO_2-N_2 isotherms with H-ZSM-5-30 and H-ZSM-5-280 at 1.0 atm. total pressure and 40°C, obtained using MTT-CPM.

This figure allows for the comparison of the adsorbent heterogeneity (*SiO_2/Al_2O_3 ratio*) to be examined for its effect on the adsorption capacities. These binary isotherms show that the adsorption capacity of H-ZSM-5-30 is higher for CO_2 and lower for N_2 than H-ZSM-5-280. This is due to the degree of heterogeneity of the adsorbent surface and therefore the interaction of the quadrupole moment of CO_2 and N_2. This interaction occurs to a higher degree with the more heterogeneous H-ZSM-5-30 adsorbent, since it contains more cations compared to H-ZSM-5-280. This increase in heterogeneity will cause more active adsorption sites to become available to CO_2 and N_2. Since CO_2 has a higher degree of polarizability and a stronger quadrupole moment, this adsorbate will occupy those sites competitively over N_2.

The experimental K_p data were also compared with the K_P's obtained by using the B_j; and C_j; coefficients obtained with the MTT-CPM in Fig. 5. When using this method, the negative values produced with the TT-CPM were removed.

The x-y equilibrium adsorption phase diagrams obtained with the proposed solution procedure are given in Fig. 9 for the H-ZSM-5-30 and H-ZSM-5-280 adsorbents. The equilibrium curve for H-ZSM-5-30 exhibits a much higher concentration of CO_2 in the adsorbed phase at low inlet concentrations than the curve for H-ZSM-5-280. This behavior shows that relatively high purity CO_2 can be obtained at low CO_2 inlet concentrations with fewer adsorption stages than those required with H-ZSM-5-280 as an adsorbent.

The equilibrium separation factor, defined by Eq. (45), can be plotted against y_1 and is shown in Fig. 10 for both adsorbents.

$$\alpha_{12} = \frac{x_1/y_1}{x_2/y_2} \tag{45}$$

Note that the mole fraction of CO_2 in the gas feed mixture is given in a log scale in this figure. The curve for H-ZSM-5-30 exhibits a maximum of 215.3 at 0.7% CO_2 in the feed gas mixture. Whereas, H-ZSM-280

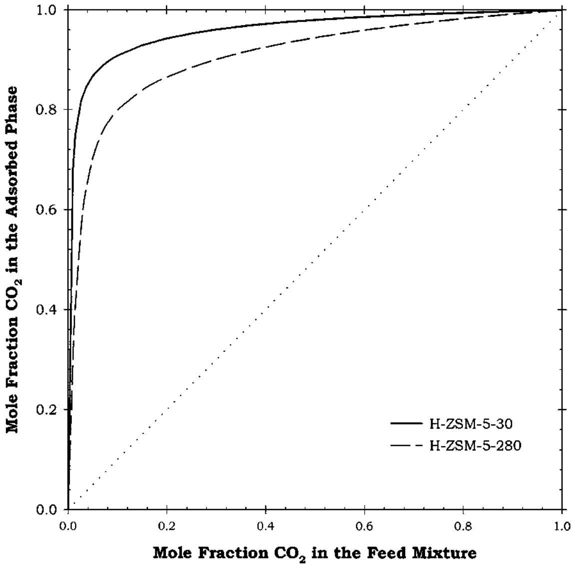


Figure 9. *x-y* equilibrium phase diagrams for CO_2-N_2 system with H-ZSM-5-30 and H-ZSM-5-280 at 1.0 atm. total pressure and 40°C, obtained using MTT-CPM.

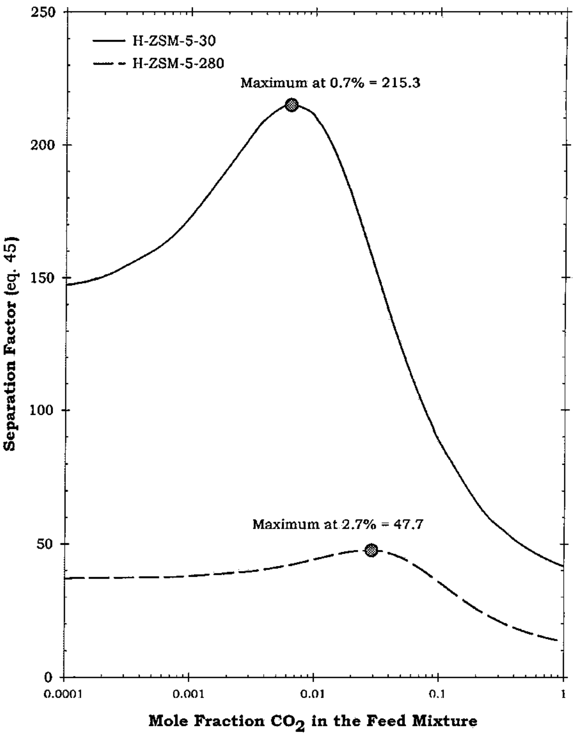


Figure 10. Equilibrium separation factor curves for CO_2-N_2 system on H-ZSM-5-30 and H-ZSM-5-280 at 1.0 atm. total pressure and 40°C, obtained using MTT-CPM.

exhibits a maximum separation factor of 47.7 at 2.7% CO_2 in the feed gas mixture.

Conclusions

In this study, the H-ZSM-5 adsorbent with different SiO_2/Al_2O_3 ratios (30 and 280) has been studied for the binary adsorption of CO_2-N_2 gas mixtures using concentration pulse chromatography. Further, a more reliable and robust solution procedure for determining the binary isotherms from binary chromatographic data has been developed.

The following conclusions have been reached:

- The polynomial approach (VV-CPM) and the method of Triebe and Tezel (1995) (TT-CPM) for determining binary isotherms should not be used for highly selective binary systems.
- The proposed solution method (MTT-CPM) for interpreting binary isotherms from chromatographic data was shown to be capable of determining binary isotherms in a system where the adsorption capacities are very different.
- The binary isotherms are very sensitive to the K_p function and the accuracy of the experimental K_p data regression.
- CO_2 adsorption capacity is higher with H-ZSM-5-30 than with H-ZSM-5-280 for both pure component and binary CO_2-N_2 systems.
- The degree of surface heterogeneity of the H-ZSM-5 adsorbent effects the pure and binary adsorption capacities of CO_2 and N_2. As the SiO_2/Al_2O_3 ratio is decreased the CO_2 capacity increases substantially and the N_2 capacity decreases slightly.
- Using the novel solution method (MTT-CPM) a maximum separation factor of 215.3 at 0.7% CO_2 in the gas feed mixture was obtained for H-ZSM-5-30 at 40°C and 1.0 atm. total pressure.
- Using the novel solution method (MTT-CPM) a maximum separation factor of 47.7 at 2.7% CO_2 in the gas feed mixture was obtained for H-ZSM-5-280 at 40°C and 1.0 atm. total pressure.

Acknowledgments

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Nomenclature

A, B, C	Parameters (cc(STP)/g/atm)
c	Concentration measured as voltage (mv)
CF	Conversion factor (cc(STP)/g/atm)
D	Constant in Eq. (4) (cc(STP)/g/atm)
f, g, h	Function
K	Effective isotherm slope (Dimensionless)
K_{p}	Effective isotherm slope (cc(STP)/g/atm)
L	Length of the column (cm)
P	Pressure (Atm.)
q	Amount adsorbed (mmol/g)
t	Time (sec)
x	Mole fraction in the adsorbed phase (Dimensionless)
y	Mole fraction in the gas phase (Dimensionless)

Greek Characters

α	Separation factor (Dimensionless)
β	Parameter in Eq. (23) (Dimensionless)
ε	Bed porosity (Dimensionless)
θ	Fractional loading (Dimensionless)
μ	Mean retention time (s)
υ	Interstitial velocity (cm/s)

Subscripts

1	Component 1
2	Component 2
D	Dead Time
i	Number of parameters in Eq. (5)
j	Numbers of parameters in Eq. (6) or (7)
m	Limiting amount adsorbed
Max	Maximum
Min	Minimum

Abbreviations

CPM	Concentration Pulse Method
GC	Gas Chromatograph
MFC	Mass Flow Controller
MTT-CPM	Modified Triebe-Tezel Concentration Pulse Method
RHS	Right Hand Side
SSR	Sum of Square Residual
TCD	Thermal Conductivity Detector
TT-CPM	Triebe-Tezel Concentration Pulse Method
VV-CPM	Van der Vlist-Van der Meijden Concentration Pulse Method

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