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Improved method for determining binary adsorption isotherms by using concentration pulse chromatography: adsorption of CO_2 and N_2 by silicalite at different pressures

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Abstract Adsorption separation of carbon dioxide from nitrogen at different system total pressures with silicalite as the adsorbent was studied by using concentration pulse chromatography. Improving the methodology for determining binary adsorption isotherms by concentration pulse method (CPM) was also the goal of this study. Binary adsorption isotherms, x–y phase diagrams and separation factor plots have been determined at 26 °C to look at the influence of pressure on the separation using concentration pulse chromatography. Available methods for determining binary adsorption isotherms using CPM have been reviewed and shown to be incapable of interpreting this particular binary system. An improved novel model has been proposed to interpret the data in this study. It has been referred to as the Kennedy-Tezel concentration pulse method (KT-CPM) and has been shown to be superior to other methods used in the literature. Results using this data were found to be consistent with the previous results in the literature. The binary isotherms for the CO_2–N_2 system show a decrease in CO_2 selectivity as total system pressure increases. The optimal separation factor for silicalite was found to increase with decreasing system pressure and decreasing mole fraction of CO_2 in the feed mixture.

Keywords Mixture adsorption · Binary adsorption isotherms · CO_2 · N_2 · Concentration pulse chromatography · Silicalite

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Nomenclature

A, B, C	Parameters used in Eqs. (4) through (10) (mmol/g/atm)
K	Dimensionless constant (dimensionless)
K_p	Dimensional constant (mmol/g/atm)
L	Length of the column (m)
n^a	Amount of gas adsorbed for pure systems (mmol/g)
P	Pressure (atm)
q	Amount adsorbed (mmol/g)
R	Universal gas constant (L atm/mole/K)
t	Time (s)
T	Temperature (K)
x	Mole fraction in the adsorbed phase (dimensionless)
y	Mole fraction in the gas phase (dimensionless)

Subscripts

A	Component A
B	Component B
i	Index
max	Maximum
min	Minimum
total	Total

Greek symbols

α	Adsorption separation factor (dimensionless)
γ	Parameter in Eq. (4) through (10)
ε	Bed porosity (dimensionless)
θ	Parameter in Eqs. (4) through (10)
μ	Mean retention time (s)
ν	Interstitial velocity (cm/s)

Abbreviations

CPM	Concentration pulse method
GC	Gas chromatograph

GHG	Green house gases
HT-CPM	Harlick and Tezel-concentration pulse method
KT-CPM	Kennedy and Tezel-concentration pulse method
MFC	Mass flow controller
MTT-CPM	Modified Tiebe and Tezel-concentration pulse method
MVV-CPM	Modified Van der Vlist and Van der Meijden-concentration pulse method
SSR	Sum of square residuals
TCD	Thermal conductivity detector

1 Introduction

Increases in green-house gases (GHG), primarily CO_2, has been a concern due to the contribution of these gases to the global warming. It is assumed that increasing concentration of carbon dioxide, mainly from the combustion of fossil fuels in automobile and industrial flue gas emissions, and landfill emissions are the major contributors to this problem totalling more than 80 % of GHG emissions (Hansen et al. 1988; Cavenati et al. 2005). The use of adsorption based separation of gases for industrial processes has been used for a long time as a cost effective method of separating gases. The emergence of new and more effective adsorbents is occurring rapidly as the emergence of green technologies support such an investment. This growth facilitates the need to characterize adsorbents for separation of greenhouse gases from air, primarily the separation of CO_2 from N_2 using adsorption.

In this study, binary adsorption of CO_2 and N_2 gas mixtures was investigated at different total pressures for different concentrations, by using silicalite as the adsorbent. Concentration pulse chromatography technique was used for determination of binary adsorption isotherms (Van der Vlist and Van der Meijden 1973; Shah and Ruthven 1977; Ruthven and Kumar 1980; Ruthven 1984; Hyun and Danner 1982, 1985; Buffman et al. 1985; Tezel et al. 1992; Triebe and Tezel 1995; Kabir et al. 1998; Harlick and Tezel 2000, 2001, 2002, 2003; Li and Tezel 2007, 2008). The use of this method for adsorbent screening is attractive as it is a quick and cost effective method for characterizing adsorbents. In this study a new model for describing the experimental data is developed, and is referred to as the Kennedy-Tezel concentration pulse method (KT-CPM). The results obtained by using this model are compared to other models suggested in the literature (Van der Vlist and Van der Meijden 1973; Triebe and Tezel 1995; Harlick and Tezel 2001).

2 Objective

The purpose of this study was to determine the binary adsorption isotherms for CO_2–N_2 binary gas mixtures with silicalite as the adsorbent at different total pressures (from 1 atm to 5 atm.) at room temperature. Improving the methodology for determining binary adsorption isotherms by concentration pulse method was also the goal of this study.

Experimental binary isotherms, x–y phase diagrams and separation factors have been determined at 26 °C for different gas compositions at different total pressures to look at the effect of pressure on separation. A new model is proposed for improved representation of the adsorption binary behaviour of CO_2–N_2 with silicalite.

3 Materials and methods

3.1 Materials

The adsorbent studied was silicalite obtained from Universal Oil Products (UOP) of Des Plaines, Illinois, USA. The silicalite was originally in the form of 1/16 inch diameter pellets. In order to maintain a column diameter to particle diameter ratio of 10:1, the pellets were crushed to a size of 25 × 50 mesh. Details of the adsorbent studied are outlined in Table 1. Adsorbate gases studied were CO_2 and N_2. Helium gas was used initially as a purge gas during the regeneration of the silicalite adsorbent before the commencement of each experimental run. Helium is assumed to be a non-adsorbing gas. Details of the gases studied are outlined in Table 2.

3.2 Experimental

A modified GOW-MAC 3300 gas chromatograph (GC) equipped with a thermal conductivity detector (TCD) was used for all experiments. A schematic diagram of the experimental apparatus is shown in Fig. 1.

Before the start of each experimental run, the column was packed with HISIV 3,000 silicalite adsorbent and installed within the gas chromatograph. The adsorbent was

Table 1 Details of the adsorbent studied

Type	Silicalite
Commercial name	MOLSIV adsorbents
Commercial number	HISIV 3000
Particle form received	1/16 inch diameter pellets
Size used in the column	Crushed 25 × 50 mesh
Content of binder	20 wt%
Particle density without pores inside	1.8 g cm^{-3}
Void fraction	0.39
Supplier	Universal Oil Products (UOP), Des Plaines, IL, USA

Table 2 Details of the gases used

Gas	Grade	Purity (%)	Supplier
CO_2	4.0	99.990	Linde Canada Ltd.
N_2	4.7	99.997	Linde Canada Ltd.
He	4.8	99.998	Linde Canada Ltd.

regenerated at 1.0 atmosphere total pressure and 350 °C under helium purge for 12–24 h. The flow rates and compositions of the carrier gases were controlled by two MKS mass flow controllers (MFC's). A mixing chamber was installed after the mass flow controllers to ensure a homogeneous mixture in the carrier gas stream. The carrier gas mixture first passed through the reference side of the thermal conductivity detector (TCD) in the GC system. It then went through the sample injection valve, which introduced a 1 cc pulse of adsorbate sample gas at atmospheric pressure into the mixed carrier gas stream. Then, the carrier and the sample passed through the packed column and the sample side of TCD, where the response of the column to the sample injection as a voltage was monitored as a function of time. Data acquisition was performed using a National Instruments based data acquisition card and Labview 7.2 on a Windows based computer. Experimental and column specifications are detailed in Table 3.

When determining binary isotherms, mixed CO_2–N_2 carriers were used in the carrier gas. For the CO_2–N_2 system, CO_2 was used as the primary gas. Samples of each gas were injected into the column at varying carrier gas concentrations from 0 to 100 mol % CO_2. It is important to note that the experimental data, K_p, represents the binary isotherm's effective slope at a particular mixture composition. As the injection volume approaches zero, the K_p

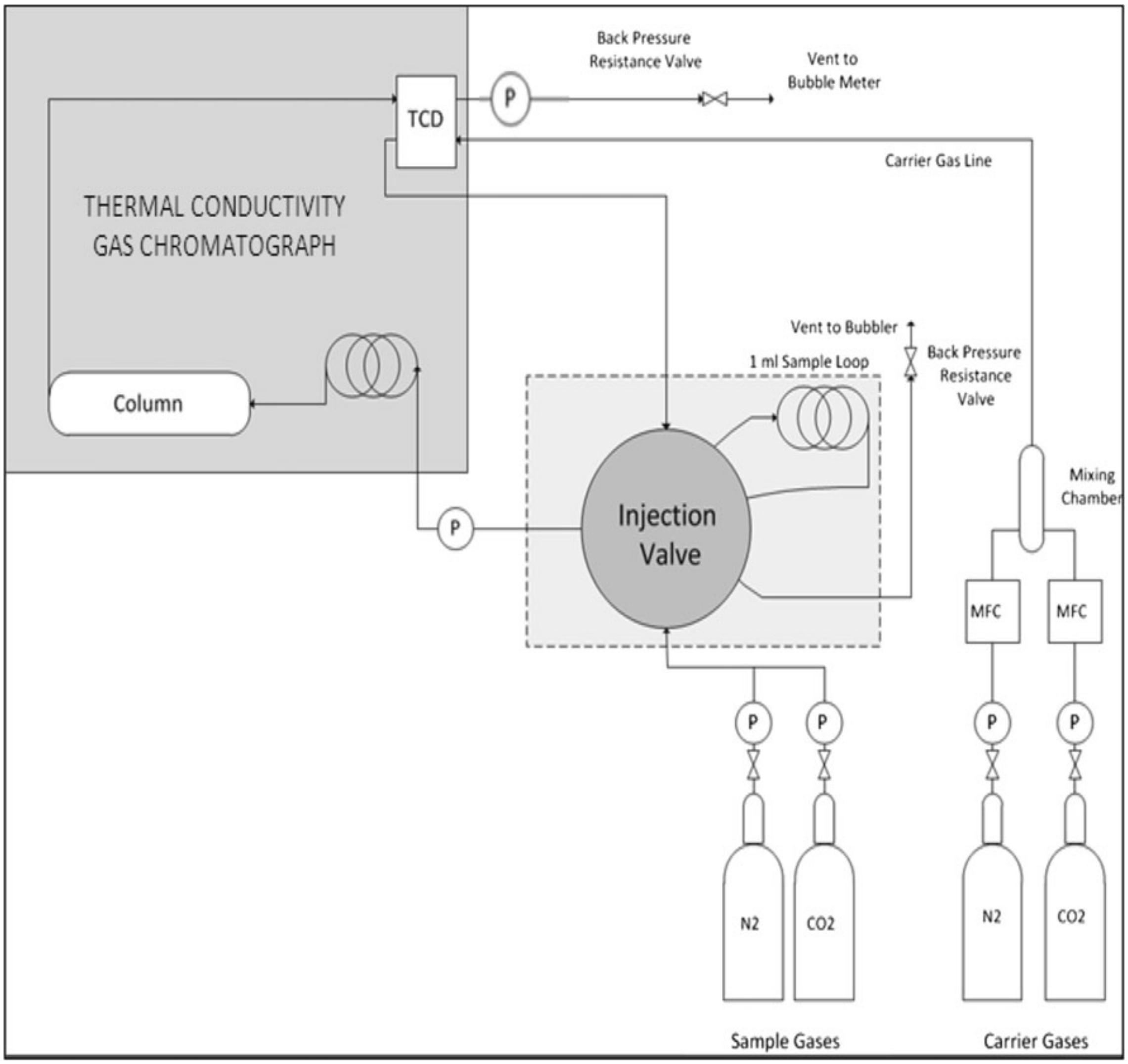

Fig. 1 Schematic diagram of the experimental set-up. *TCD* thermal conductivity detector; *MFC* mass flow controller; *P* pressure gauge

Table 3 Experimental and column specifications

Column length	10.0	cm
Column inner diameter	0.7	cm
Total flow rate	30–60	mL/min @ ambient conditions
Total pressure	1,2,3,4,5	atm
Temperature	26	°C
Regeneration temperature	350	°C
Regeneration pressure	1	atm
Regeneration time	12–24	h

values found by both injections should be identical. When CO_2 is injected, the mixture composition in the carrier gas increases slightly in CO_2 concentration. When N_2 is injected, the mixture composition decreases slightly in CO_2 concentration. Therefore, in this study, when possible both adsorbates were injected into the mixed carrier gas and the average of the retention times was used for the determination of K_p for each concentration of CO_2 in the gas mixture. The pressure drop across the column was measured with two pressure gauges on the inlet and outlet of the adsorbent packed column. The pressure drop was found to be negligible for all flow regimes and system pressures.

4 Methodology

4.1 Pure isotherms

Pure CO_2 and N_2 adsorption capacities by silicalite were determined by using data from the work of Li and Tezel (2008) using a three parameter temperature dependent Toth function for 26 °C. In this study, isotherms from 40 to 100 °C are given and the temperature dependent Toth model was found to represent their data very well. Therefore, this model was used in this study to determine the pure component adsorption isotherms of CO_2 and N_2 gases with silicalite at 26 °C. These isotherms are shown in Fig. 2.

4.2 Binary isotherms

For the determination of binary gas mixture behaviour, concentration pulse chromatography was used. This technique involves injecting a pulse of sample gas into the carrier gas steam which passes through a column packed with the adsorbent. The response of the adsorbent to the pulse disturbance is monitored by measuring concentration of the sample gas (c) as a function of time (t) at the outlet of the column. The mean retention time (μ) can be determined experimentally from this response peak, by using a dimensionless constant, K, which gives the slope of the adsorption isotherm, at the partial pressure of the sample gas in the carrier gas. If the carrier gas does not contain any sample gas, then this constant, K, gives the Henry's Law constant, which is the initial slope of the adsorption isotherm as pressure approaches zero for the sample gas. On the other hand, if the carrier gas contains the sample gas in a binary mixture together with a non-adsorbing gas, going through the chromatographic column, then this constant gives the slope of the adsorption isotherm for the sample gas, at the partial pressure of the sample gas in the carrier mixture. The constant, K, can be determined from the corrected first moment of the response peak from the relationship below (Van der Vlist and Van der Meijden 1973; Shah and Ruthven 1977; Ruthven and Kumar 1980; Hyun and Danner 1982, 1985; Buffman et al. 1985, 1999; Mason and Buffman 1996; Tezel et al. 1992; Triebe and Tezel 1995; Kabir et al. 1998; Harlick and Tezel 2000, 2001, 2003; Li and Tezel 2007, 2008):

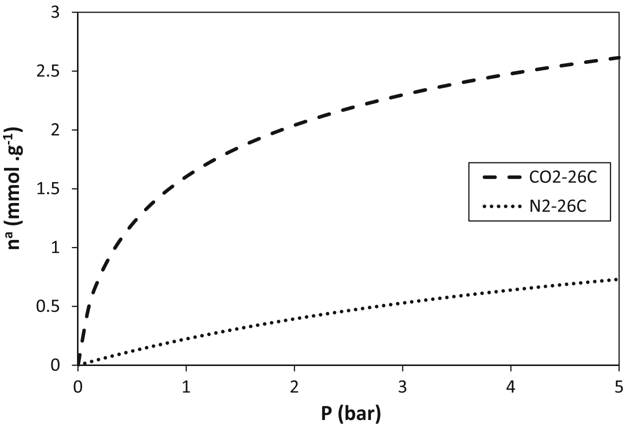

Fig. 2 Pure component adsorption Isotherms of CO_2 and N_2 with silicalite at 26 °C using information given in Li and Tezel (2008)

$$\mu = \frac{\int_0^\infty c(t-\mu_D)dt}{{}_0^\infty cdt} = \frac{L}{v}\left[1 + \frac{(1-\varepsilon)K}{\varepsilon}\right] \tag{1}$$

where c is the adsorbate concentration measured at the outlet of the column, ε is the bed porosity, L is the length of the column, t is the time, and μ_D is the mean system dead time. The dead time is the measure of the time required for the sample injection to travel through the empty volume of the tubing from the injection valve to the detector.

The dimensionless constant, K, is related to the dimensional equilibrium constant K_p through the following system-dependent relationship:

$$K_p = \frac{K}{RT\rho_P} \tag{2}$$

where T is the absolute temperature and ρ_P is the adsorbent density without the void space in the pellets.

Although this K_p value is generally used to represent the Henry's Law constant where the adsorption isotherm is

Table 4 Concentration pulse chromatographic methods used in the literature (Li and Tezel 2007, 2008)

MVV-CPM (modified Van der Vlist and Van der Meijden—concentration pulse method) Van der Vlist and Van der Meijden 1973; Harlick and Tezel 2000	
4-parameter function	$K_p = A_0 + A_1 y_1 + A_2 y_1^2 + A_3 y_1^3$
Isotherm slope functions	$dq_1/dP_1 = B_0 + B_1 y_1 + B_2 y_1^2$
	$dq_2/dP_2 = C_0 + C_1 y_1 + C_2 y_1^2$
Binary isotherm functions	$q_1 = \left[B_0 y_1 + \left(\frac{B_1}{2}\right) y_1^2 + \left(\frac{B_2}{3}\right) y_1^3\right] P_T$
	$q_2 = \left[C_0(1 - y_1) + \left(\frac{C_1}{2}\right)(1 - y_1^2) + \left(\frac{C_2}{3}\right)(1 - y_1^3)\right] P_T$
MTT-CPM (modified Triebe and Tezel-concentration pulse method) Triebe and Tezel 1995; Harlick and Tezel 2000	
5-parameter function	$K_p = A_{-1}(\beta + y_1) + A_0 + \frac{A_1}{(\beta + y_1)} + \frac{A_2}{(\beta + y_1)^2}$
Isotherm slope functions	$dq_1/dP_1 = B_0 + \frac{B_1}{(\beta + y_1)} + \frac{B_2}{(\beta + y_1)^2}$
	$dq_2/dP_2 = C_0 + \frac{C_1}{(\beta + y_1)} + \frac{C_2}{(\beta + y_1)^2}$
Binary isotherm functions	$q_1 = [B_0 y_1 + B_1 \ln[(\beta + y_1)/\beta] + B_2 y_1/\beta(\beta + y_1)] P_T$
	$q_2 = [C_0(1 - y_1) - C_1 \ln[(\beta + y_1)/(\beta + 1)] + C_2(1 - y_1)/[(\beta + 1)(\beta + y_1)]] P_T$
HT-CPM (Harlick and Tezel-concentration pulse method) Harlick and Tezel 2001	
5-parameter function	$K_p = A_1 + A_2 y_1 + A_3 y_1^2 + A_4 \ln\lvert y_1 + \lambda\rvert$
Isotherm slope functions	$dq_1/dP_1 = B_1 + 2B_2 y_1 + B_3/(\lvert y_1 + \lambda\rvert)$
	$dq_2/dP_2 = C_1 + 2C_2 y_1 + C_3/(\lvert y_1 + \lambda\rvert)$
Binary isotherm functions	$q_1 = \left[B_1 y_1 + B_2 y_1^2 + B_3 \ln\lvert(y_1 + \lambda)/\lambda\rvert\right] P_T$
	$q_2 = \left[C_1(1 - y_1) + C_2(1 - y_1^2) - C_3 \ln\lvert(y_1 + \lambda)/(1 + \lambda)\rvert\right] P_T$

linear, it could also represent the slope of the pure isotherm at a certain pressure value (Suzuki et al. 1997; Radeke et al. 1981; Zhong and Meunier 1993). Therefore, if these K_p values are determined at different binary carrier gas compositions of two different components for which one of them is adsorbed and the other one is not adsorbed, then they can be used to determine the pure component adsorption isotherms for the adsorbed component by integrating these K_p values.

In the binary carrier gas scenario, these experimentally determined K_p values are related to the slope of the adsorption isotherms of the two components in the carrier gas as follows (Ruthven and Kumar 1980; Shah 1988; Shah and Ruthven 1977; Li and Tezel 2005):

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

where dq_1/dP_1 and dq_2/dP_2 are the slopes of the individual components' binary isotherms. In the case of the binary carrier gas mixtures where one of the components is not adsorbed, the value of dq_2/dP_2 is going to be a constant. Therefore, if Eq. (3) is integrated with respect to y_1, after representing P_1 and P_2 in terms of y_1 ($P_1 = P_{\text{total}} y_1$ and $P_2 = P_{\text{total}}(1\text{-}y_1)$), the pure component adsorption isotherm for the adsorbed component, (q_1 vs. P_1), can be determined.

In the case of the binary carrier gas mixtures where both of the components are adsorbed, neither derivative in Eq. (3) may be considered constant, since both components are simultaneously adsorbed. Therefore, the experimental K_p data represents the contribution of both components in the mixture. Several models for interpreting K_p data from the literature are listed in Table 4.

The applicability of these functional forms proves to be difficult for highly selective binary systems for which the difference in adsorption capacity is quite large. As mole fraction of CO_2 in the mixture increases, the experimental K_p values are observed to change dramatically at low concentrations which proves to be very difficult to model. Several models have been proposed to represent the experimental data. These proposed models were found not to represent the experimental data adequately in this study. Van der Vlist and Van der Meijden (1973) proposed a polynomial approach, however this method was found to show large oscillations for some binary systems (Harlick and Tezel 2003). The function proposed by Triebe and Tezel (1995) underestimated the experimental values for the binary isotherms. Harlick and Tezel (2001) improved upon the work of Triebe and Tezel (1995), and showed that HT-CPM was highly versatile and represented highly selective binary systems well (Harlick and Tezel 2002, 2003; Li and Tezel 2008). These three methods were used initially to see their applicability to the experimental data. Although the applicability of HT-CPM to the experimental data was the best among these three models looked at, it still did not represent the data well. This will be discussed under Sect. 6 of this study for Fig. 3. Therefore, a new model was developed during the present study.

5 Numerical methods

A non-linear regression was performed in order to determine the parameters of the K_p function that best represent the experimental data. In order to determine the parameters given by the different models used (KT-CPM, HT-CPM, MTT-CPM and MVV-CPM), a non-linear equation solver was used. The solver in MS Excel was used to determine the values for the B_i and C_i parameters by a non-linear constrained optimization technique.

6 Results and discussions

The binary isotherms for CO_2 and N_2 on silicalite were first studied at 1 atm total pressure and 26 °C. After regenerating the silicalite sample under a He purge, K_p values were determined by increasing the CO_2 mol % in the CO_2–N_2 carrier gas from 0 to 100 %. After attaining full equilibrium for each y_{CO2} concentration, indicated by a steady baseline response by the TCD output, a series of 1 cc sample injections into the carrier gas stream were performed. The responses of the column to these injections were monitored and the average K_p values for each CO_2 concentration was determined using Eqs. (1) and (2). The K_p experimental data for 1 atm total pressure was plotted graphically as a function of y_{CO2} and are shown in Fig. 3 as data points. It should be noted that more experimental data points were obtained to ensure more accuracy when y_{CO2} is between 0 and 0.2 since K_p decreased very rapidly in this range.

Non-linear regression curves were performed on the experimental K_p data according to HT-CPM, MTT-CPM and MVV-CPM and the results of these regressions are given in Fig. 3. As can be seen from this figure, neither MTT-CPM nor MVV-CPM model was found to adequately represent the experimental data, especially at low

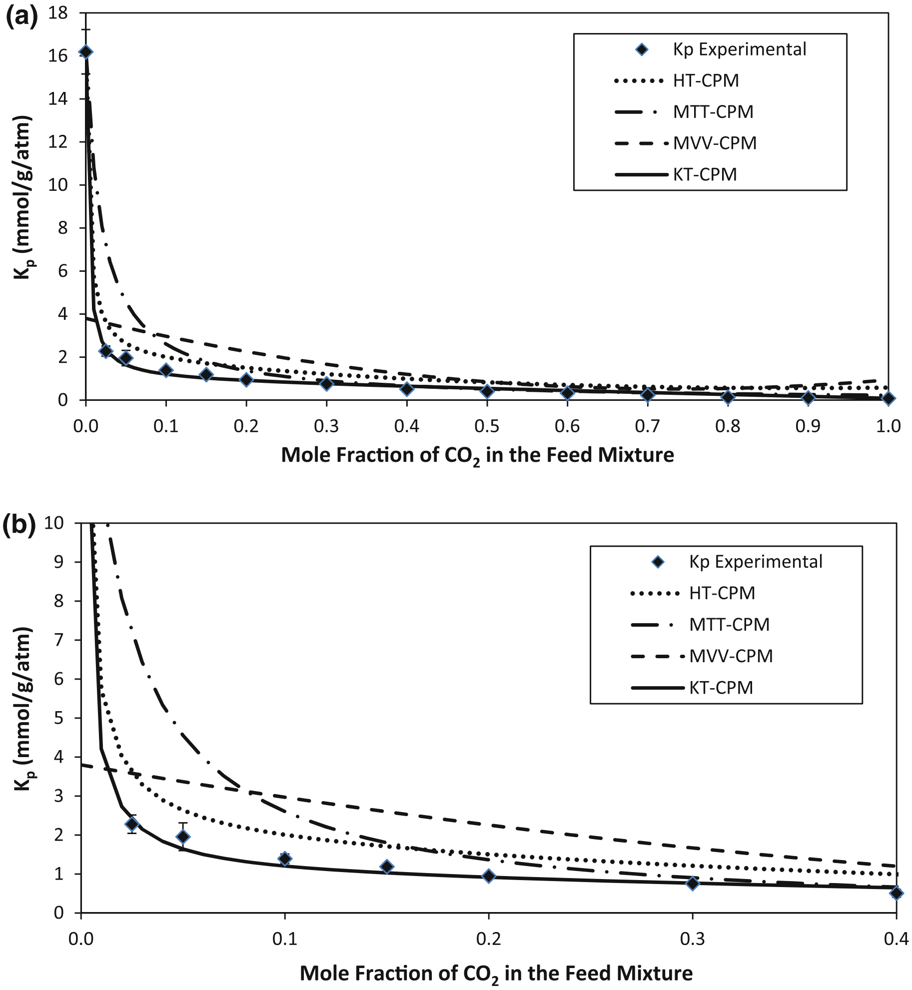

Fig. 3 Regressions for CO_2–N_2 binary K_p data with silicalite by KT-CPM, HT-CPM, MTT-CPM and MVV-CPM at different carrier gas compositions at 1 atm total pressure. **a** Entire range of carrier gas composition **b** Low CO_2 composition in the carrier gas

concentrations of CO_2 where the K_p value decreases dramatically with increasing CO_2 in the carrier gas. The HT-CPM was found to overestimate the K_p values which will introduce error in the binary isotherms. Although the HT-CPM was found to fit the binary CO_2–N_2 silicalite at 40 °C (Li and Tezel 2008), at lower system temperatures, binary N_2–CO_2 adsorption becomes more selective in favor of CO_2. This is indicated by a sharp initial decline in K_p values over a small increase in y_{CO2}, as such the HT-CPM method did not fit this data well. It was found that these functions contained several parameters that did not represent the experimental data properly. Since our goal is to fit the experimental data as best as possible, another simpler function is proposed to model highly selective binary systems and should be applicable across a wide range of temperatures and binary adsorption conditions.

6.1 An improved novel function

In this study a simple model with five variables is proposed and was found to provide a very good representation for the experimental data:

$$K_p = A_1 \ln(|y_1 + \gamma|) + A_2 e^{(\theta y_1)} + A_3 y_1 \tag{4}$$

where $\gamma > 0$ and $\theta > 0$. Derivative of Eq. (4) yields the corresponding isotherm slope functions (Harlick and Tezel 2000):

$$\frac{dq_1}{dP_1} = \frac{B_1}{(|y_1 + \gamma|)} + B_2 e^{(\theta y_1)} + B_3 \tag{5}$$

$$\frac{dq_2}{dP_2} = \frac{C_1}{(|y_1 + \gamma|)} + C_2 e^{(\theta y_1)} + C_3 \tag{6}$$

Integration of Eqs. (5) and (6) results in the following binary isotherm equations:

$$q_1 = P_T\left[\mathrm{B}_1 \ln\left(\left|\frac{y_1+\gamma}{\gamma}\right|\right) + \frac{B_2}{\theta}\left(e^{(\theta y_1)} - 1\right) + B_3 y_1\right] \tag{7}$$

$$q_2 = P_T\left[-\mathrm{C}_1 \ln\left(\left|\frac{y_1+\gamma}{1+\gamma}\right|\right) + \frac{C_2}{\theta}\left(e^{\theta} - e^{(\theta y_1)}\right) + C_3(1-y_1)\right] \tag{8}$$

Substituting Eqs. (5) and (6) into Eq. (3) yields K_p as a function of both isotherm slope functions:

$$K_p = (1-y_1)\left[\frac{B_1}{(|y_1+\gamma|)} + B_2 e^{(\theta y_1)} + B_3\right] + y_1\left[\frac{C_1}{(|y_1+\gamma|)} + C_2 e^{(\theta y_1)} + C_3\right] \tag{9}$$

Sum of the square residuals (SSR) corresponds to the sum of the squares of differences between the K_p that can be written from Eq (9) and the experimental K_p value obtained at different concentrations of CO_2 gas in the mixture as follows:

$$SSR = \sum_{y=y_{\min}}^{y=y_{\max}} \left\{K_p(\text{experimental}) - \left((1-y_1)\left[\frac{B_1}{(|y_1+\gamma|)} + B_2 e^{(\theta y_1)} + B_3\right] + y_1\left[\frac{C_1}{(|y_1+\gamma|)} + C_2 e^{(\theta y_1)} + C_3\right]\right)\right\}^2 \tag{10}$$

By minimizing SSR, (i.e. the differences between the experimental and model values of K_p calculated by Equ (9)), values of B_i and C_i parameters can be determined. The minimization of the SSR should not be performed with only the K_p experimental data, since a number of possible solutions would exist for the determination of B_i and C_i coefficients. Harlick and Tezel (2001) introduced several constraints that are imposed on their equation to ensure the solution reflects what is physically occurring in the system.

The individual isotherm slopes should always be greater than zero across the entire range of y_1 since no maximums should be seen in the isotherms (Calleja et al. 1998).

$$\frac{dq_1}{dP_1} > 0 \quad \text{and} \quad \frac{dq_2}{dP_2} > 0 \tag{11}$$

The K_p function should pass through the largest experimental K_p values which occurs at $y_1 = 0$, since the initial isotherm slope is based on this value. For highly selective binary systems, as y_1 approaches 1, K_p becomes very small. To avoid negative K_p predictions as y_1 approaches 1, the function should pass through the experimental binary K_p data as $y_1 \rightarrow 1$. These constraints are outlined in Eq. (12) and Eq. (13) below:

$$K_p(Experimental)|_{y_1=0} = K_p(Equation\ 9)|_{y_1=0} \tag{12}$$

$$K_p(Experimental)|_{y_1=1} = K_p(Equation\ 9)|_{y_1=1} \tag{13}$$

These constraints were considered when determining the B_i and C_i coefficients by minimizing the SSR indicated by Eq. (10) by using a constrained nonlinear regression. With these parameters, the K_p curve is then defined from Eq. (9) and the binary isotherms are determined by Eqs. (7) and (8). The data obtained with this equation set is referred to as KT-CPM (Kennedy-Tezel-concentration pulse method).

The K_p vs y_1 curve was generated by using the B_i and C_i that were determined from the minimization of the corresponding objective function for the KT-CPM and given in Fig. 3 in comparison to experimental K_p values, as well as other models from the literature. In this figure, on top of the full range of compositions (Fig. 3a), the low CO_2 composition range (Fig. 3b) is shown to highlight the differences for different models. As can be seen from this figure,

Table 5 SSR Values Comparing K_p function representation for experimental data

Method	Sum of square residuals (SSR)
KT-CPM	0.3
HT-CPM	4.8
MTT-CPM	32.8
MVV-CPM	166.3

KT-CPM represents the experimental data more accurately than the other models for the binary K_p data for CO_2–N_2 with silicalite.

To quantify the difference in the non-linear regressions for these four concentration pulse methods, SSR values were used and are shown in Table 5. The KT-CPM resulted in a better fit for the regression of the experimental K_p data for the CO_2–N_2 binary system with silicalite as indicated by the lowest SSR value. Therefore it should produce binary isotherms that more accurately resemble the adsorption process as described by the experimental data. Since the KT-CPM resulted is the best representation of the experimental CO_2–N_2 binary system K_p data, it was used for the higher total pressure experiments.

To further assess the applicability of this new functional form over a broad range of temperatures and binary systems the KT-CPM was assessed against the other objective functions to our CO_2–CH_4 binary adsorption data on silicalite at 100 °C previously reported by Li and Tezel, 2007. As can be seen from Fig. 4, KT-CPM represented the K_p vs the composition data the best, compared to other CPM methods attempted for this system, as well.

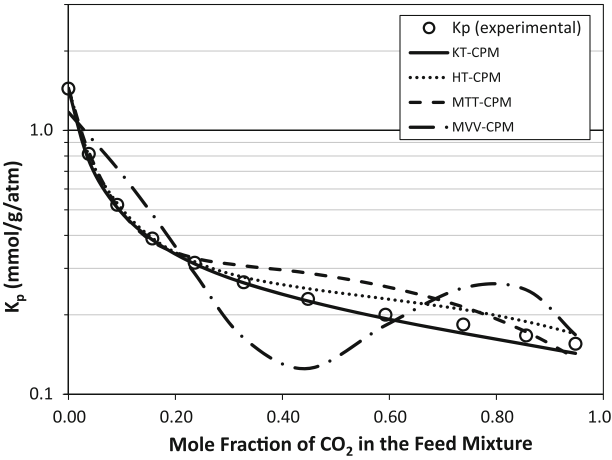

Fig. 4 Regressions for CO_2–CH_4 binary K_p with silicalite data reported in Li and Tezel 2007 by KT-CPM, HT-CPM, MTT-CPM & MVV-CPM at different carrier gas compositions at 1 atm total pressure and 100 °C

6.2 Binary CO_2–N_2 system

KT-CPM was shown to provide the most versatile fit and is used to describe the binary CO_2–N_2 system and multiple system pressures. Table 6 gives the values of the KT-CPM parameters outlined in Eq. (9) for five different system pressures from 1 to 5 atm used in this study.

The experimental CO_2–N_2 K_p data as a function of CO_2 mol fraction in the carrier gas at different system total pressures are outlined in Fig. 5.

The binary adsorption isotherms for CO_2–N_2 with silicalite at 26 °C for different compositions of the gas mixture were obtained by using KT-CPM model at five different pressures from 1 to 5 atm and are given in Fig. 6. It was observed that silicalite adsorbent had significantly higher capacity for CO_2 than for N_2 which was already observed from pure component isotherms from literature (Li and Tezel 2008). Adsorption capacity increases with increasing pressure, as expected. The largest increase in adsorption capacity with pressure was observed from 1 to 3 atm and rate of increase decreased steadily as pressure increased. When y_{CO2} increases the adsorption capacity of CO_2 increases whereas the adsorption capacity of N_2 decreases. For both gases, this occurs rapidly from 0.0 to 0.2 y_{CO2} in the gas mixture. As the fraction of CO_2 in the gas mixture increase, the amount of N_2 adsorbed approaches 0.

The mole fractions of each component in the adsorbed phase, x_i have been calculated using the binary adsorption capacities ($x_A = q_A/(q_A + q_B)$ and $x_B = q_B/(q_A + q_B)$) and the corresponding x–y phase diagrams at different pressures studied are given in Fig. 7. Within the pressure range studied, lower pressure data gave a better separation since the curve is furthest from the 45° line. Therefore, for the adsorption separation of CO_2 and N_2 gases with silicalite, lower pressures should be chosen as operating pressure.

6.3 Separation factors

The primary requirement for an economic adsorption separation process is an adsorbent with sufficiently high selectivity, capacity, and longevity. Since the performance of most adsorption processes are dependent on adsorption equilibrium selectivity, separation factors under ideal conditions, as well as the ones obtained from binary isotherms have been considered.

Ideal separation factor is simply given by the ratio of the amounts adsorbed calculated using the pure component adsorption isotherms as follows:

$$\propto_{ideal,A/B} = \frac{n_A^a}{n_B^a} \tag{14}$$

As mentioned in the Pure Isotherms section under Methodology in this paper, adsorption capacities of pure

Table 6 Values for the KT-CPM parameters (in units of mmol/g/atm) used in Eqs. (5) through (10)

Parameters	System pressure				
	1 atm	2 atm	3 atm	4 atm	5 atm
B_1	1.004E + 00	8.222E − 01	5.922E − 01	3.816E − 01	3.124E − 01
C_1	8.023E − 11	2.902E − 06	7.233E − 06	6.025E − 06	2.733E − 04
B_2	1.520E − 08	7.258E − 04	9.258E − 03	1.000E − 02	3.006E − 01
C_2	3.995E − 02	1.308E − 02	1.018E − 02	2.000E − 02	1.934E − 02
B_3	4.276E − 02	2.412E − 02	1.912E − 02	1.700E − 02	1.567E − 02
C_3	2.808E − 03	3.013E − 03	3.464E − 03	4.206E − 03	4.750E − 03
γ	5.323E − 03	1.000E − 02	1.000E − 03	1.000E − 01	5.000E − 02
θ	5.023E − 02	9.300E − 02	8.000E − 02	4.500E − 02	4.200E − 02

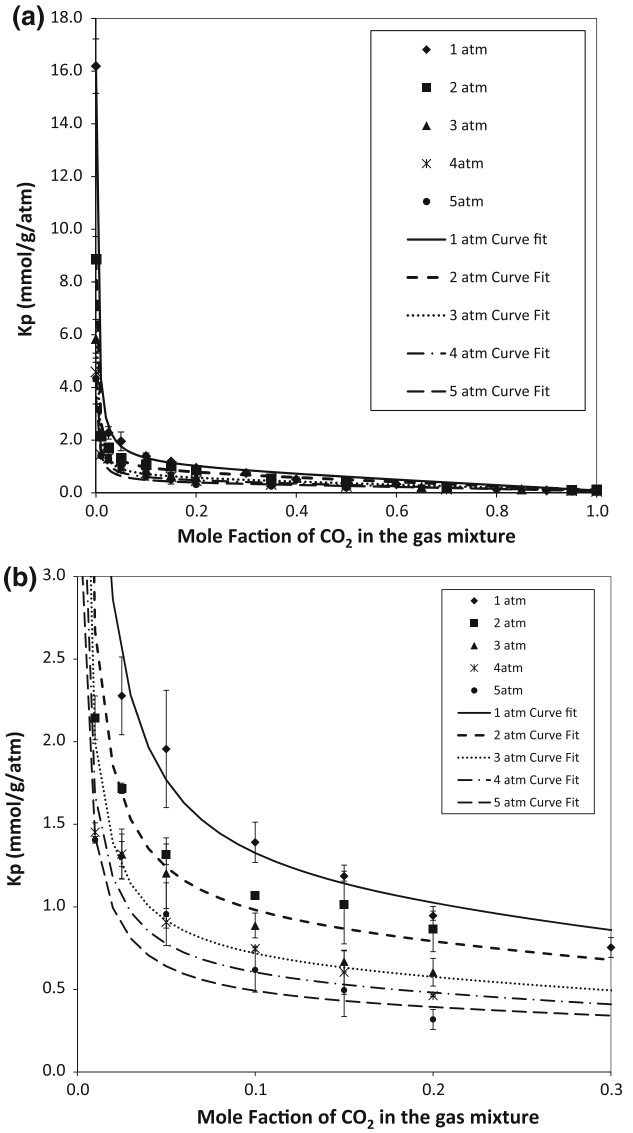

Fig. 5 Experimental CO_2–N_2 binary K_p data for silicalite at 26 °C at different total pressures. The K_p curves are defined by Eq. (9) for KT-CPM. **a** Entire range of carrier gas composition **b** Low CO_2 composition of carrier gas

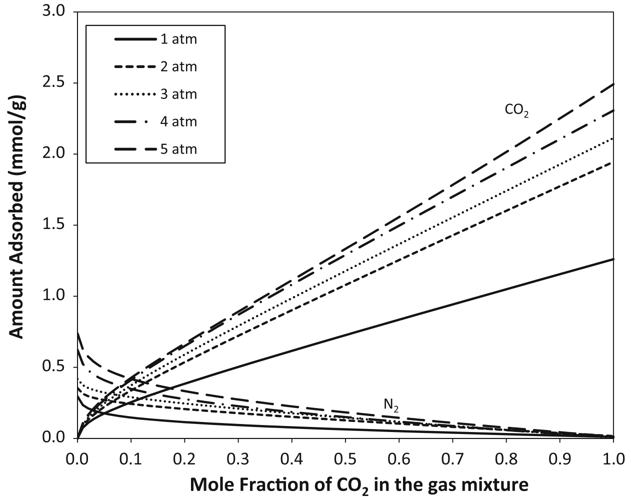

Fig. 6 Binary CO_2–N_2 isotherms for silicalite at 26 °C at different total pressures defined by Eqs. (7) and (8) using KT-CPM

CO_2 and N_2 gases with silicalite at different pressures have been calculated at 26 °C by applying the temperature dependent Toth isotherm model to the pure component data given in the literature at 40, 70 and 100 °C (Li and Tezel 2008). Fig. 8 shows these ideal separation factors for CO_2/N_2 mixture on silicalite at 26 °C at different total pressures.

Separation factors were also calculated by using the experimental binary adsorption isotherm data obtained in this study as follows:

$$\propto_{A/B} = \frac{x_A/x_B}{y_A/y_B} \tag{15}$$

where x_a, x_b, y_a, and y_b are the mole fraction of components A and B in the adsorbed and the gas phases at equilibrium. These separation factors are also given in Fig. 8 and compared to the ideal ones obtained from pure component isotherms. Both separation factors tend to decrease with increasing pressure. However, the ones obtained from the binary mixtures would be more realistic, as they reflect competitive adsorption on the surface of the adsorbent.

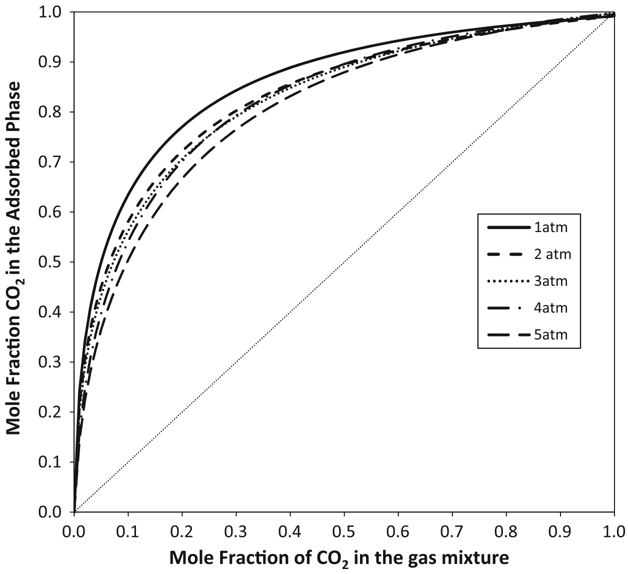

Fig. 7 Binary CO_2–N_2 x–y equilibrium adsorption phase diagrams for silicalite at 26 °C at different total pressures obtained from KT-CPM

Binary isotherms are definitely necessary to predict separation factors more accurately.

The selectivity is the best at lower pressures and low concentrations of CO_2 in the gas mixture, as can be seen in Fig. 8. The separation factor is observed to decline with increasing y_{CO2} in the gas mixture. For practical applications, the silicalite studied shows good separation factors for mole fraction of CO_2 in the gas mixture between the range 0.1 and 0.2 for flue gas applications.

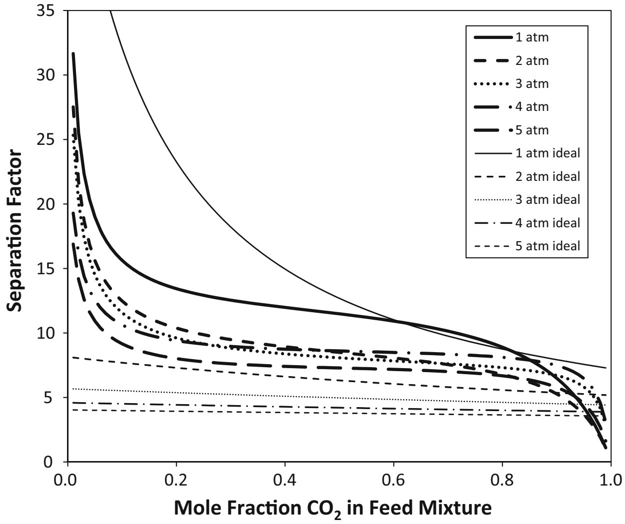

Fig. 8 Separation factor plots for CO_2–N_2 with silicalite at 26 °C as a function of gas phase composition at different total pressures obtained from binary isotherms determined by KT-CPM. Ideal separation factors for CO_2/N_2 on silicalite at 26 °C are obtained from pure component isotherms, using pure component data given in Li and Tezel (2008)

7 Conclusions

1. A new model (KT-CPM) was proposed for the representation of the experimental data, to be used for the determination of binary adsorption isotherms. This model was successfully used to represent the experimental binary behaviour of CO_2 and N_2 gases with silicalite as the adsorbent at 26 °C as determined in this study, as well as the experimental binary behaviour of CO_2 and CH_4 gases with silicalite as the adsorbent at 100 °C from the literature.
2. Among the four concentration pulse chromatographic methods used, the model best represented the data used in this study was given by KT-CPM. The HT-CPM, MTT-CPM, and MVV-CPM were not satisfactory to describe the adsorption binary behaviour of CO_2/N_2 with silicalite at 26 °C. This conclusion also applies to the adsorption binary behaviour of CO_2/CH_4 with silicalite at 100 °C from the literature.
3. Although adsorption capacities for N_2 and CO_2 with silicalite tend to increase with increasing pressure, separation factor decreased with increasing total pressure. Therefore pressure is an important factor to consider for the separation of this binary system, particularly at low mole fractions of CO_2.
4. Competing binary adsorption leads to higher selectivity for CO_2/N_2 separation compared to the ones predicted from the pure component isotherms at higher pressures.
5. The selectivity of silicalite is good for the CO_2/N_2 separation, particularly at low CO_2 mol fractions in the gas mixture and at lower system total pressures.

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