Research Article

Decoupled multicomponent potential theory of adsorption of gas mixtures

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Abstract
In this paper, we present a new version of the multicomponent potential theory of adsorption model. The proposed modification makes a clear distinction between adsorbent dependent parameters from adsorbate dependent ones. This leads to a better understanding of the physical significance of the parameters. The interdependence between pure isotherms is eliminated, which means that each component can be individually finely adjusted. This new approach was tested against 14 datasets for a total of 510 experimental mixture adsorption data of CH_4, CO_2, N_2, H_2, O_2, H_2S, C_2H_6, C_3H_6, and C_3H_8 on activated carbons, MOF, and zeolites. A slight improvement of 4.67% on excess adsorption predictions was found, leading to an overall average error of 6.97% for total excess adsorption and 15.30% for combined mixtures and components excess adsorption predictions.

Keywords Adsorption · Mixture adsorption · Multicomponent adsorption · Potential theory of adsorption · MPTA · Density functional theory

1 Introduction

In the standard definition of the Multicomponent Potential Theory of Adsorption model (MPTA), some fitting parameters are interdependent, which requires the simultaneous fitting of pure isotherms. This situation results from the choice of minimizing the number of adjustable parameters of the model. The proposed reinterpretation of the model eliminates this interdependence by introducing new adjustable parameters, specific to each gas component, which ultimately simplify the model's adjustment and understanding. Both approaches were tested against 14 different experimental datasets from the literature [1–13]. The datasets include 510 individual mixture adsorption measurements, in which 72 are ternary mixtures adsorption. The fluids considered are CH_4, CO_2, N_2, H_2, O_2, H_2S, C_2H_6, C_3H_6, and C_3H_8. The adsorbent materials are activated carbons (Filtrasorb-400, Norit-R1, AP-360, BPL), metal-organic frameworks (MOF-5, CuBTC), and zeolites (4A, 5A, 13X, ZSM-5, Mordenite). The experiments were performed both volumetrically and gravimetrically at temperatures ranging from 297 to 473 K. The datasets were chosen based on the quality and availability of the experimental data and the wide range of adsorptive gases, type of material, and adsorption temperature.

Since there are many variables and symbols used in this paper, Table 1 regroups all of the definitions. Also, each time the superscript *i* or *j* is used, it refers to the particular mixture component.

1.1 Pure gas MPTA model

When talking about adsorption, it is useful to define the *bulk phase* as the region far from the adsorbent where the

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Table 1 Symbols and definitions

Variable	Definition
μ_B	Chemical potential of the bulk phase (J/mol)
μ_{Ad}	Chemical potential of the adsorbed phase (J/mol)
ε	Adsorbent surface potential (J/mol)
ρ_B	Fluid density in the bulk phase (mol/L)
ρ_{Ad}	Fluid density in the adsorbed phase (mol/L)
ε_0	Characteristic energy of adsorption (J/mol)
z	Microporous volume (cm^3/g)
z_0	Limiting micropore volume (cm^3/g)
β	Heterogeneity parameter
N_{ex}	Excess (Gibbs) adsorption (mol/kg)
x_B	Bulk phase molar fraction (mol^i/mol$_{\mathrm{Tot}}$)
x_{Ad}	Adsorbed phase molar fraction (mol^i/mol$_{\mathrm{Tot}}$)
T	Fluid temperature (K)
$S_{i/j}$	Selectivity of component i over component j

fluid is unaffected by the adsorbent material. Conversely, the *adsorbed phase* will represent the region near the surface where the fluid is significantly affected by the presence of the adsorbent material.

The potential theory of adsorption (PTA) is a two-parameter thermodynamic model developed by Shapiro and Stenby [14] based on the pore filling approach of Polanyi's theory of adsorption [15]. The PTA model was generalized to MPTA for gas mixtures adsorption by Shapiro, Stenby, and Monsalvo [14, 16]. The MPTA model supposes that the fluid–surface interaction is entirely described by a local potential field ε, generated by the surface [17, 18]. A common choice for this purpose is the Dubinin–Radushkevich–Astakhov [19–21] potential (DRA), given by

$$\varepsilon(z) = \begin{cases} \varepsilon_0\left(\ln \frac{z_0}{z}\right)^{1/\beta} & \text{if } 0 \le z \le z_0, \\ 0 & \text{if } z > z_0, \end{cases} \tag{1}$$

where ε_0 and z_0 are the *characteristic energy of adsorption* and the *limiting micropore volume*, respectively. β is a parameter which is usually interpreted as a quantification of the heterogeneity of the adsorbent [22, 23]. Usually, for activated carbon, the parameter β is set to 2, while ε_0 and z_0 are determined by fitting the model to experimental data (see [24] for details). The ratio z/z_0 represents the fraction of the microporous volume associated with an energy $\varepsilon(z)$.

The MPTA model is defined by [14, 25]

$$\mu_B(T, \rho_B) = \mu_{\mathrm{Ad}}(T, \rho_{\mathrm{Ad}}) - \varepsilon, \tag{2}$$

where μ_B and ρ_B are, respectively, the chemical potentials and the fluid density in the bulk phase, while μ_{Ad} and ρ_{Ad} are the local chemical potentials and fluid density in the adsorbed phase. The bulk phase properties are assumed to be constant while the adsorbed phase properties vary with position [14]. Using Eq. (2), the adsorbed phase's local thermodynamic properties are uniquely determined from properties of the bulk phase and the values of the parameter z_0, ε_0 and β through the potential ε. Correspondance between gas pressure and density is carried out through an equation of state. The Nist REFPROP is used here for density and chemical potential calculations [24, 26]. In the following, we will omit the temperature dependence since T is assumed to be constant.

Equation (2) is inverted to obtain $\rho_{\mathrm{Ad}}(z)$ from the chemical potentials. The (Gibbs) excess adsorption N_{ex} (which is what is experimentally measured) is then calculated from

$$N_{\mathrm{ex}}(\rho_B) = \int_0^{z_0} \left(\rho_{\mathrm{Ad}}(z) - \rho_B\right) \mathrm{d}z. \tag{3}$$

Optimal values for the fittings parameters are obtained by minimizing the difference $N_{\mathrm{ex}}(\rho_B) - N_{\mathrm{ex}}^{exp}(\rho_B)$ for pure gases isotherms. The fitting is performed by a Python implemented Levenberg–Marquardt algorithm [27].

1.2 Gas mixtures

For gas mixtures with M components, the simplest approach is to consider that each fluid component i is affected by its own surface potential

$$\varepsilon^i(z) = \begin{cases} \varepsilon_0^i\left(\ln \frac{z_0}{z}\right)^{1/\beta} & \text{if } 0 \le z \le z_0, \\ 0 & \text{if } z > z_0, \end{cases} \quad i = 1 \dots M, \tag{4}$$

where ε_0^i refers to a given component. The parameters z_0 and β are generally assumed to be common to all mixture components [28]. Equation (2) now becomes a non-linear coupled system of M equations

$$\mu_B^i(\rho_B, x_B^i) + \varepsilon^i(z) - \mu_{\mathrm{Ad}}^i(\rho_{\mathrm{Ad}}(z), x_{\mathrm{Ad}}^i(z)) = 0, \quad i = 1 \dots M, \tag{5}$$

in which x^i is the molar fraction of a component i of the mixture. Due to the adsorbent material's selectivity, the local molar fraction $x_{\mathrm{Ad}}^i(z)$ will vary in the adsorbed phase, whereas the molar fraction of the bulk phase x_B^i is constant. Here again, the mixture densities are obtained from pressure measurements, mixture molar fraction, and the REFPROP software.

Equations (5) are solved for $\rho_{\mathrm{Ad}}(z)$ and $x_{\mathrm{Ad}}^i(z)$. The excess (Gibbs) adsorption of each component in the mixture is obtained from

$$N_{\mathrm{ex}}^i(\rho_B) = \int_0^{z_0} \left(\rho_{\mathrm{Ad}}(z) x_{\mathrm{Ad}}^i(z) - \rho_B x_B^i\right) \mathrm{d}z, \quad i = 1 \dots M. \tag{6}$$

Finally, the total adsorbed amount is the sum of the contributions of each component

$$N_{\mathrm{ex}}(\rho_B) = \sum_{i=1}^{M} N^i_{\mathrm{ex}}(\rho_B). \tag{7}$$

A key feature of the MPTA model is that the fitting parameters ε_i and z_0 (and possibly β) are solely obtained from *pure gas adsorption isotherms* in order to predict multicomponent adsorption [14, 16].

Up to this point, the described model corresponds to the conventional MPTA model. The next section describes the proposed decoupled MPTA model, starting with a conceptual justification in Sect. 2.1 followed by a formal definition in Sect. 2.2, and a discussion of both models in Sect. 2.3.

2 Decoupled MPTA: independent z_0 and β parameters

2.1 Conceptual justification of the new model

Using unique values of z_0 and β for all fluids components is generally justified by the fact that those parameters are mostly properties of the adsorbent material. Moreover, this allows the reduction of the fitting parameters to $M + 1$(or $M + 2$ if β is also fitted).

However, there are some disadvantages to this approach. Firstly, all the pure gases must be refitted each time that a single component is modified. For example:

- Let us consider a binary mixture of gas A and B. The model must be simultaneously fitted on pure isotherms for gas A and B to obtain ε^A_0, ε^B_0, z_0, and β.
- Now, if a new mixture of gas A and C is considered, parameters ε^A_0, z_0, and β cannot be reused.
- The model must be refit using the new A and C isotherms to obtain ε'^A_0, ε^C_0, z'_0, and β'.

Since ε^i_0 and z_0 change every time a component of the mixture is changed, the interpretation of those parameters as *characteristic energy of adsorption* of component *i* and *limiting micropore volume* becomes less clear. Indeed, at least the characteristic energy of adsorption is expected to be constant for the pure adsorption of a pair adsorbate–adsorbent. This is not the case in the conventional MPTA approach.

Secondly, physically speaking, any interaction is characterized by its *strength* and its *range*, as so for the fluid–surface potential ε. For the sake of the discussion, let us consider the simple graphite adsorbent structure where the surface is essentially constituted of isotropic 2D carbon planes. In that case, the microporous volume z is just a specific surface area times a distance to the surface. From the nearly crystalline structure of the graphite, we can infer that this specific surface area is constant, leaving z being essentially a variable of the distance to the surface. This implies that z_0 will also be the product of the same characteristic surface times a characteristic distance to the surface. Any characteristic distance to a surface surely represents a range of interaction, and then, functionally speaking, this means that z_0 represents the range of the fluid–surface interaction. This leaves ε_0 representing the strength of the interaction.

For disorganized adsorbent structures, the situation is more complicated, but z still can be interpreted as a measure of the distance to the surface time a specific surface. However, this time, the specific surface is given by some complicated geometrical average of the porous surface.

The upshot is that z_0 is linked to the range of the interaction, and then, it makes much more sense to consider different z_0 for different pure gases rather than the same z_0 for all gases.

Also, in the perspective of complex mixtures with many components, it will be even more challenging to fit all these pure isotherms simultaneously rather than fitting each component individually.

Finally, one of the far-reaching goals is to be able, under certain conditions, to extrapolate MPTA parameters from one adsorbent to another one. For instance, would it be possible to predict adsorption on one adsorbent considering another adsorbent's experimental dataset sharing similar properties? The first step in this direction is to separate the fluid–fluid part of the interaction from the fluid–surface part, and this is precisely what the new model does. Without this separation, any attempt to extrapolate from one adsorbent to another will suffer from excessive fluid–fluid interaction.

2.2 Decoupled MPTA definition

From all the considerations of Sect. 2.1, individual values of z_0 and β can be introduced from minor modifications of the fluid–surface potential which now reads

$$\varepsilon^i(z) = \begin{cases} \varepsilon^i_0 \left(\ln \frac{z^i_0}{z}\right)^{1/\beta^i} & \text{if } 0 \le z \le z^i_0, \\ 0 & \text{if } z > z^i_0, \end{cases} \quad i = 1 \dots M. \tag{8}$$

Now, ε^i_0, z^i_0, and β^i are parameters specific to pure gas *i*. The modified potential (8) induces no modification to the system of equation (5).

For excess adsorption, the situation is more complicated. It was said earlier that the adsorbed phase is the region where the fluid is affected by the presence of the adsorbent surface. This definition now needs to be clarified and extended to the indirect effects of other gases components. Indeed, let us consider the region $z_0^i < z \leq z_0^j$. In that region, the surface potential $\varepsilon^i(z) = 0$ since $z > z_0^i$, which seems to indicate that the gas *i* is unaffected by the presence of the adsorbent. However, the component *j* will be affected by the presence of the adsorbent in that region since $\varepsilon^j(z) \neq 0$ as $z \leq z_0^j$. However, the fact that the component *j* is affected by the adsorbent will modify its local molar fraction $x_{\text{Ad}}^j(z)$. Since $\sum_i x_{\text{Ad}}^i = 1$, local molar fractions are not independent and then, x_{Ad}^i will be affected indirectly by the adsorption of component *j*.

The easiest way to see this is by looking at the molar fraction of component *i* in the range $z_0^i < z \leq z_0^j$, which would have been constant if component *i* was not affected at all. Figure 1 shows this situation for a mixture of 72% CH_4 / 28% CO_2 at bulk pressure of 8.3 MPa and temperature of 318.2 K (experimental data were taken in [1]). In the region $z_0^i < z \leq z_0^j$ (the light gray area), we see that the molar fraction of CH_4 vary with *z* even if the surface potential $\varepsilon^{CH_4}(z)$ vanish in that region. At $z = z_0^i$, the CH_4 starts to interact with the surface through non-vanishing $\varepsilon^{CH_4}(z)$, and we observe a change in the reads of the molar fraction. The sharp variation of the molar fraction at $z = z_0^i$ is obviously not physical. It came from the DRA potential, which is not smooth at $z = z_0^i$.

It is also interesting to take a look at the fluid density in that adsorbed phase region. Figure 2 shows the density profile of the mixture in the same conditions. This figure shows each component's contribution to the total density, such that the total fluid density is simply the sum of the individual component density. Here again, the sharp variation of fluid density is not physical but is instead an artifact caused by the DRA potential.

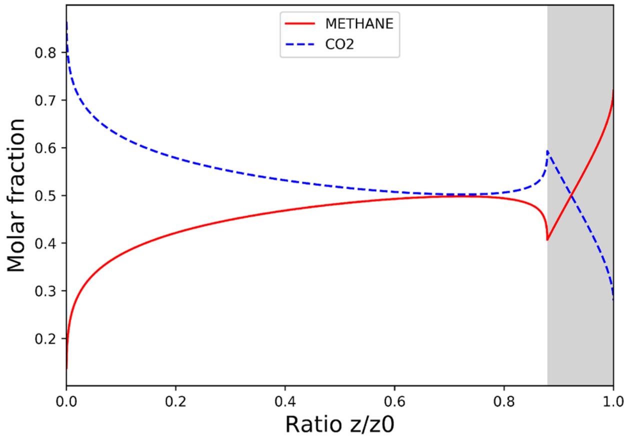

Fig. 1 Adsorbed phase molar fraction given by the new model for a 72% CH_4 / 28% CO_2 mixture (bulk pressure of 8.3 MPa) on Calgon F-400 activated carbon at 318.2K. The gray area represents the region where CH_4 surface potential vanishes, but not the CO_2 ones

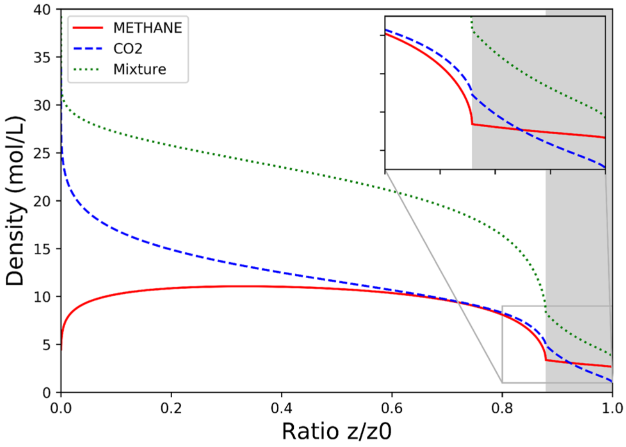

Fig. 2 Density profile of the adsorbed phase given by the new model for a 72% CH_4 / 28% CO_2 mixture (bulk pressure of 8.3 MPa) on Calgon F-400 activated carbon at 318.2 K. The gray area represent the region were CH_4 surface potential vanishes, but not the CO_2 ones

The key point of this discussion is to realize that regardless of the component, the adsorbed phase's fluid properties differ from the ones of the bulk phase for $z < z_0^{max}$. For $z \geq z_0^{max}$, the integral vanishes, and then, the excess (Gibbs) adsorption for each component is

$$N_{\text{ex}}^i(\rho_B) = \int_0^{z_0^{max}} \left(\rho_{\text{Ad}}(z)x_{\text{Ad}}^i(z) - \rho_B x_B^i\right)\text{d}z, \quad i = 1\ldots M, \quad (9)$$

where z_0^{max} is simply the maximum value in $\{z_0^i\}$. The condition that $\varepsilon^i(z) = 0$ if $z > z_0^i$ is required in the implementation since the integration now goes from 0 to z_0^{max} for all components.

Remark that the indirectly–interacting region of a component (the region $z_0^i < z \leq z_0^j$ for component *i*) will generate a negative contribution to the total component adsorption. Indeed, Figs. 1 and 2 show a decreasing molar fraction compared to the bulk phase, and a nearly constant component density which mean that $\rho_{\text{Ad}}(z)x_{\text{Ad}}^i(z) - \rho_B x_B^i < 0$ in the indirectly–interacting region. The behavior of the component *i* in the region $z_0^i < z \leq z_0^j$ represents a sort of emerging phenomena generated by the mixture's intrinsic nature.

Finally, with gas mixtures adsorption, it is quite useful to compare the adsorbent's components' affinity. This will be done by the use of the *selectivity S* of a component over another one. The selectivity of component *i* over component *j* is defined as [6]

$$S_{i/j} = \frac{N^i_{\mathrm{ex}} x^j_B}{N^j_{\mathrm{ex}} x^i_B}. \tag{10}$$

2.3 Standard MPTA versus decoupled MPTA

One of the main distinctions between standard and decoupled models is that in the later, the distinctive range of interaction of different gas species is taken into account through the introduction of individual z^i_0 parameters. As discussed in the previous section, the implementation of those individual z^i_0 parameters requires some precautions since non-interacting gases can still be indirectly affected by neighbor gases.

Decoupled model needs to be fitted on $3M$ parameters (ε^i_0, z^i_0, and β^i) instead of $M+2$ parameters (ε^i_0, z_0, and β) for standard MPTA. However, the new form of the fluid–surface potential (8) decouples the fitting parameters for each component. In fact, the $3M$ needed parameters split into M individual three parameters fit. Once optimal ε_0, z_0 and β values have been found for a pure gas, there will be no need to refit the model on this gas. Those individual parameters encapsulate all the required information of a pure gas about the fluid–surface interaction, whatever the mixture considered. In other words, the decoupled model makes a clear cut between the fluid–surface interactions, which are governed by the fitting parameters (ε_0, z_0, and β), and the fluid–fluid interactions, which are entirely governed by the EOS (the REFPROP in our case) as it should be. Moreover, it is easier to do M individual three parameters fit than a single $M+2$ parameters fit.

Individual values of z^i_0 for the MPTA model have been previously used in the literature [29–31], where improvement of 3% and 2–3% compared to common z_0 value have been reported. We report a nearly 5% improvement in adsorption prediction using individual values of z^i_0, which confirm previously found results, although different adsorbent and adsorbate were used (liquid adsorbent were used in [30]). In [31], the differences between individual values of z^i_0 are treated as regions of the adsorbed phase that are only accessible to one component species. In this work, we looked at the differences between individual values of z^i_0 as differences in the range of gas–surface interaction. This means that all the space is accessible to all the component species. Moreover, in this work, the β parameter of the DRA potential is treated as an individually adjustable parameter when β is generally set to 2 in other work [29–31].

2.4 Experimental uncertainties consideration

To understand the limitation of the model, it is crucial to use accurate experimental data. Whether a volumetric or gravimetric method is used, the variables that are experimentally measured are the total excess adsorption $N^{\mathrm{Tot}}_{\mathrm{ex}}$ (considering the pressure drop or increase of mass) and the bulk phase molar fraction x_B (generally using gas chromatography). The "experimental" adsorbed phase molar fraction will be noted χ^i_{Ad} and corresponds to the average proportion of component i in the adsorbed phase. χ^i_{Ad} is then calculated from the initial and equilibrium states, and the components adsorption are calculated from

$$N^i_{\mathrm{ex}} = N^{\mathrm{Tot}}_{\mathrm{ex}} \chi^{i,exp}_{\mathrm{Ad}}. \tag{11}$$

The point here is that both $N^{\mathrm{Tot}}_{\mathrm{ex}}$ and χ^i_{Ad} are tainted by experimental uncertainties such that

$$\left(\delta N^i_{\mathrm{ex}}\right)^2 = \left(\delta N^{\mathrm{Tot}}_{\mathrm{ex}} \chi^i_{\mathrm{Ad}}\right)^2 + \left(N^{\mathrm{Tot}}_{\mathrm{ex}} \delta \chi^i_{\mathrm{Ad}}\right)^2. \tag{12}$$

Dividing both side by $\left(N^i_{\mathrm{ex}}\right)^2$, we obtain the relative error propagation equation

$$\left(\frac{\delta N^i_{\mathrm{ex}}}{N^i_{\mathrm{ex}}}\right)^2 = \left(\frac{\delta N^{\mathrm{Tot}}_{\mathrm{ex}} \chi^i_{\mathrm{Ad}}}{N^i_{\mathrm{ex}}}\right)^2 + \left(\frac{N^{\mathrm{Tot}}_{\mathrm{ex}} \delta \chi^i_{\mathrm{Ad}}}{N^i_{\mathrm{ex}}}\right)^2. \tag{13}$$

When considering a mixture of different component behavior, it is not uncommon to come across experimental conditions where N^i_{ex} is very small compared to $N^{\mathrm{Tot}}_{\mathrm{ex}}$. Since $\delta \chi^i_{\mathrm{Ad}}$ is not necessarily that small, the second term of (13) can become quite large. Then, it is possible to end up with unacceptably large relative uncertainty. To illustrate this, let us consider a case encounter in the dataset where $N^{\mathrm{Tot}}_{\mathrm{ex}} \sim 6.2$ mmol/g and $\delta \chi^i_{\mathrm{Ad}} \sim 0.002$. In that particular case, $N^i_{\mathrm{ex}} \sim 0.02$ mmol/g, and then, the last term of (13) gives an unacceptable relative uncertainty of $\sim 60\%$ on N^i_{ex}. From now on, the experimental data with relative uncertainty greater than 25% will be discarded from the fits. This 25% threshold, although arbitrary, represents a good balance between data accuracy and data retention for the fits.

For an experimental dataset with unknown experimental uncertainties, an experimental error of 1% on $N^{\mathrm{Tot}}_{\mathrm{ex}}$ and 1% on the smallest x^i_B will be assumed to evaluate relative uncertainties. Those assumptions are fairly representative of the usual experimental uncertainties and were established from the experimental dataset with given experimental errors.

3 Results

Table 2 shows the considered datasets. It gives the mean pure fit error of both standard MPTA and the new implementation of the model, which will be labeled "new MPTA"

Table 2 Pure gas mean fit for all the datasets considered

Adsorbent	Adsorbate	T(K)	Mean pure fit error	
			Std MPTA[a]	New MPTA[b]
AC Calgon F-400 [1]	$CH_4/N_2/CO_2$	318.2	2.82%	1.91%
AC Norit R1 [2]	$CH_4/N_2/CO_2$	298	3.17%	1.22%
AC AP3-60 [3]	$N_2/CO_2/H_2$	298	2.63%	2.83%
AC BPL [4]	CH_4/C_2H_6	297, 301.4	5.03%	1.46%
MOF-5 [5, 6]	$CH_4/N_2/H_2/CO_2$	297	8.91%	3.60%
CuBTC [6]	$N_2/H_2/CO_2$	297	2.96%	2.45%
Zeolite-4A [7]	C_3H_8/C_3H_6	423/473	4.94%	2.40%
Zeolite-5A [8]	O_2/N_2	296	2.82%	1.31%
Zeolite-5A [9]	CH_4/N_2	303/323	6.14%	3.90%
Zeolite-13X [10]	CH_4/N_2	303/323	7.04%	3.36%
Zeolite-13X [11]	CO_2/N_2	298/318	3.07%	0.95%
Zeolite-ZSM-5 [11]	CO_2/N_2	298/318	3.72%	2.63%
Zeolite-NaX [12]	CO_2/CO	323/373	5.46%	2.24%
Zeolite H-Mordenite [13]	$CO_2/H_2S/C_3H_8$	303	7.25%	3.00%
Average			4.71%	2.38%

[a] Std MPTA mean pure fit error refers to the mean absolute deviation between experimentally measured excess adsorptions and those computed by (3) using (2) and (1)

[b] New MPTA mean pure fit error refers to the mean absolute deviation between experimentally measured excess adsorptions and those computed by (3) using (2) and (8) with individual z_0^i, ε_0^i and β^i parameters

even if this is more of a reinterpretation of the MPTA rather than a new model.

In the following sections, the quality of the model predictions will be evaluated through the *overall mean error* (the average over all the N_{ex}^i or selectivity values) and the *overall increased performance*. Since the mixture system does not always have the same quantity of experimental data, the overall mean error is not necessarily the average of each system's mean error. The calculation is weighted to ensure an equal contribution for each experimental data in the overall mean error. The overall increased performance measures the accuracy of the new MPTA predictions compared to the standard MPTA model.

The MPTA model gives a point-to-point prediction of mixture adsorption based on temperature, pressure, and bulk phase molar fraction. Therefore, it is not usually possible to predict mixture adsorption between two experimental data points because the bulk phase molar fraction is not usually constant. This explains why the adsorption lines cannot be smoothed in Figs. 3, 4, 5 and 6, and why no isotherms are given. Constant bulk phase molar fraction solves this issue.

3.1 AC Calgon F-400

First, we consider the adsorption of CH_4, CO_2, N_2, and their binary mixtures on the bituminous-coal-based activated carbon Filtrasorb-400 12x40 mesh (Calgon Carbon Co.), which has a microporous volume of 0.4950 cm^3/g, and a BET surface of 850 m^2/g [1]. Filtrasorb-400 possesses a high carbon content (88.65%), which simplifies the characterization of the fluid–solid interactions. The material was regenerated under vacuum at 110 °C for 2 days before being used. The measurements were performed volumetrically at 318.2 K with pressure up to 13.8 MPa. Adsorption of pure gases was carried out twice to guarantee reproducibility. Both runs were used to fit the MPTA model. Overall, the new model underestimates the mixture adsorption by 3.32%, while the pure isotherms are overestimated by 2%.

Table 3 gives the mean error between the prediction of both approaches, while Fig. 3 shows some of the new model results.

3.2 AC Norit R1

Binary and ternary mixtures of CH_4, N_2, and CO_2 are considered on activated carbon Norit R1 Extra which has a microporous volume of 0.3511 cm^3/g, and a BET surface of 1407.3 m^2/g [2]. The measurements were performed gravimetrically at 298 K over a pressure ranging from 93 kPa to 6.077 MPa. Overall, the new model underestimates the mixture's adsorption by 7.68%, while the pure isotherms are underestimated by 0.82%.

Table 3 Comparison of standard and new MPTA models on Filtrasorb-400 at 318.2 K and pressure up to 13.8 MPa

System		Mean error (%)			
		Std MPTA[a]		New MPTA[b]	
		N^i_{ex}	Select	N^i_{ex}	Select
CH_4/CO_2	CH_4 component	25.37	–	14.03	–
	CO_2 component	6.50	52.59	7.88	27.47
	Mixture	2.21	–	3.16	–
CH_4/N_2	CH_4 component	3.30	6.94	7.83	11.82
	N_2 component	6.39	–	5.40	-
	Mixture	3.36	–	4.13	–
N_2/CO_2	N_2 component	12.95	–	9.98	–
	CO_2 component	6.05	23.70	8.63	21.29
	Mixture	1.49	–	3.30	–
Overall mean error		7.48	27.48	7.12	20.02
Overall increased performance		–	–	4.8	27.1

113 experimental data points.

[a] Std MPTA mean pure fit error refers to the mean absolute deviation between experimentally measured excess adsorptions and those computed by (3) using (2) and (1)

[b] New MPTA mean pure fit error refers to the mean absolute deviation between experimentally measured excess adsorptions and those computed by (3) using (2) and (8) with individual z^i_0, ϵ^i_0, and β^i parameters

Table 4 gives the mean error between the prediction of both approaches, while Fig. 4 shows some selected results of the new model.

3.3 AC AP3-60

Binary mixtures of CO_2, N_2, and H_2 are considered on activated carbon Envirocarb AP3-60 (Chemviron Carbon) [3], which has a BET surface of 1000 m^2/g (Chemviron Carbon). Envirocarb AP3-60 is a cylindrical 3-mm pellet activated carbon, and the material was regenerated under vacuum at 150 °C for 8 h between experiments. The measurements were performed gravimetrically at 298 K over a pressure ranging from 400 kPa to 11.86 MPa. Overall, the new model underestimates the mixture adsorption by 9.19%, while the pure isotherms are underestimated by 1.22%.

Table 5 gives the mean error between the prediction of both approaches.

3.4 AC BPL

Binary mixtures of CO_2 and C_2H_6 are considered on activated carbon BPL 6x16 mesh (Calgon Carbon Co.) [4], which has a microporous volume of 0.630 cm^3/g and a BET surface of 1200 m^2/g [32]. Before entering the adsorption vessel, gasses were dried using packed columns of 5A molecular sieves. The measurements were performed volumetrically at 297 K and 301.4 K with pressure up to 2.5 MPa. Overall, the new model underestimates the mixture adsorption by 9.76%, while the pure isotherms are underestimated by 0.06%.

Table 6 gives the mean error between the prediction of both approaches.

3.5 MOF-5

Binary mixtures of CH_4, N_2, and CO_2 and ternary mixture of H_2, CH_4, N_2, and CO_2 are considered on metal-organic framework MOF-5 powder (Basolite Z100-H), which has a microporous volume of 1.31 cm^3/g and a BET surface of 3054 m^2/g [5, 6]. The material was activated under vacuum at 125 °C for at least 8 h. The measurements were performed volumetrically at 297 K with pressure up to 1.5 MPa. Overall, the new model underestimates the mixture adsorption by 9.86%, while the pure isotherms are underestimated by 1.60%.

Table 7 gives the mean error between the prediction of both approaches, while Fig. 5 shows some selected results of the new model.

3.6 CuBTC

Ternary mixtures of H_2, N_2, and CO_2 are considered on metal-organic framework CuBTC (Basolite C300), which has a microporous volume of 0.66 cm^3/g and a BET surface of 1556 m^2/g [6]. The material was activated under vacuum at 125 °C for at least 8 h. The measurements were performed volumetrically at 297 K with pressure up to 1 MPa. Overall, the new model underestimates the mixture adsorption by 31.93%, while the pure isotherms are overestimated by 0.89%.

Table 8 gives the mean error between the prediction of both approaches.

3.7 Zeolite-4A

Binary mixtures of C_3H_8 and C_3H_6 are considered on Zeolite-4A [7], which has a microporous volume of 0.2462 cm^3/g and a BET surface of 559.13 m^2/g [33]. The measurements were performed volumetrically at 423 K and 473 K over a pressure ranging from 85 kPa to 145 kPa. Overall, the new model underestimates the mixture adsorption by 1.13%, while the pure isotherms are overestimated by 0.32%.

Table 9 gives the mean error between the prediction of both approaches.

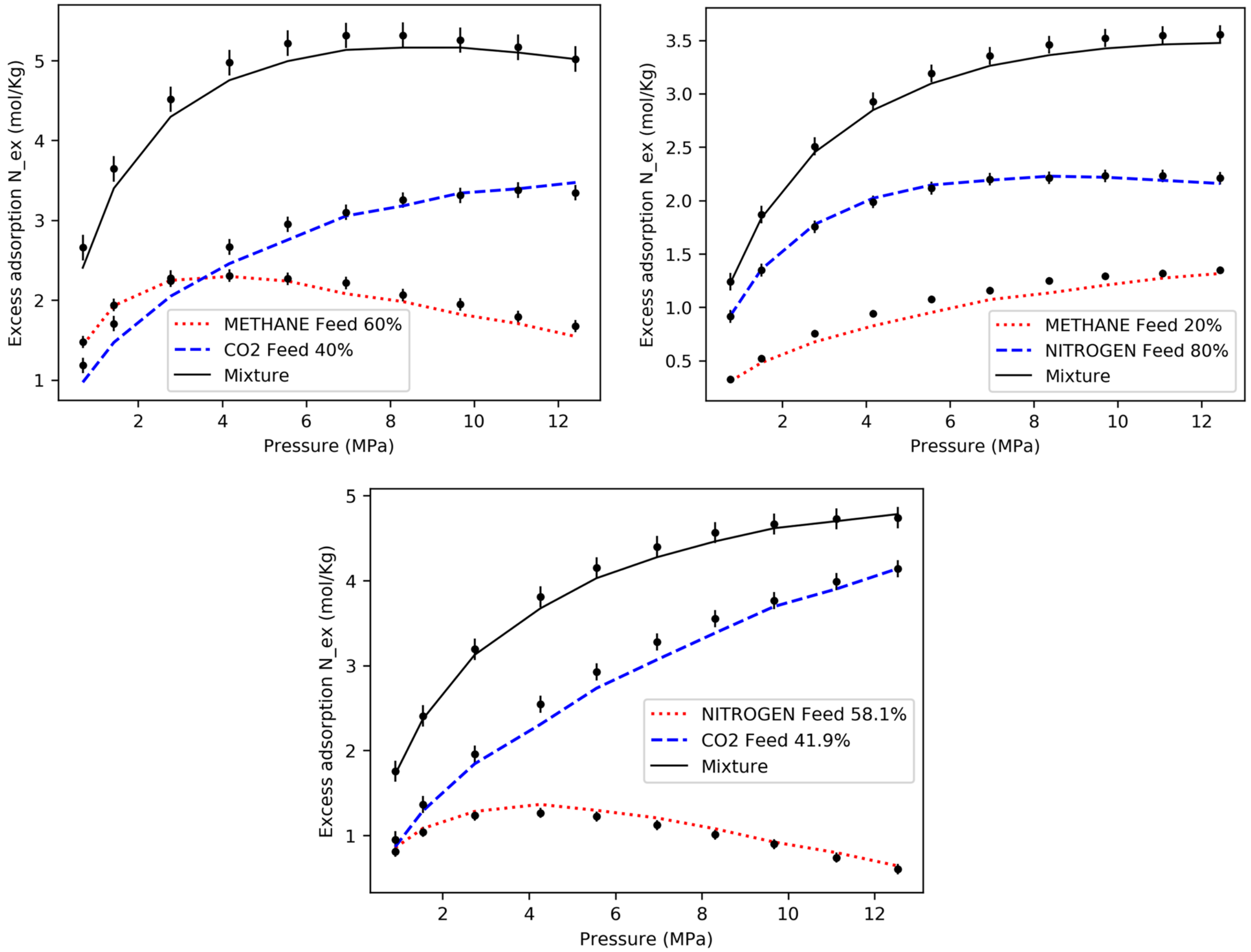

Fig. 3 New MPTA model selected examples of binary mixtures on Filtrasorb-400 at 318.2 K and pressure up to 13.8 MPa

3.8 Zeolite-5A

Binary mixtures of O_2 and N_2 are considered on a commercial Zeolite-5A 8 × 10 mesh (Tosoh Corporation) [8], which has a microporous volume of 0.198 cm^3/g and a BET surface of 561.1 m^2/g [34]. The material was regenerated under vacuum at 400 °C. The measurements were performed volumetrically at 296 K over a pressure ranging from 23 to 921 kPa. Low-pressure measurements of pure gases were collected using a Micromeritics ASAP 2000. Overall, the new model underestimates the mixture adsorption by 4.68%, while the pure isotherms are underestimated by 1.07%.

Table 10 gives the mean error between the prediction of both approaches, while Fig. 6 shows some selected results of the new model.

Another experiment was carried out using 5A Zeolite material. This time, binary mixtures of CH_4 and N_2 are considered on Zeolite-5A 3mm spherical particle (Zeochem Co.), which has a reported BET surface of 457–600 m^2/g [9]. The material was initially activated at 300 °C, and regenerated after each measurement under vacuum at 250 °C for 6 h. The measurements were performed volumetrically at 303 K and 323 K over a pressure ranging from 98 to 916 kPa. Overall, the new model overestimates the mixture adsorption by 1.34%, while the pure isotherms are underestimated by 3.03%.

Table 11 gives the mean error between the prediction of both approaches.

3.9 Zeolite-13X

Binary mixtures of CH_4 and N_2 are considered on Zeolite-13X (Zeochem Co.) [10], which has a microporous volume of 0.21 cm^3/g and a BET surface of 164.3 m^2/g [35]. The polar properties of the Zeolite-13X suggest a strong

Table 4 Comparison of standard and new MPTA models on Norit-R1 at 298 K and pressure up to 6 MPa

System		Mean error (%)			
		Standard MPTA[a]		New MPTA[b]	
		N^i_{ex}	Select	N^i_{ex}	Select
CH_4/CO_2	CH_4 component	36.88	–	36.32	–
	CO_2 component	9.07	40.97	7.71	39.83
	Mixture	5.79	–	5.66	–
CH_4/N_2	CH_4 component	7.86	8.93	12.02	16.89
	N_2 component	7.00	–	6.13	–
	Mixture	4.93	–	5.36	–
CO_2/N_2	CO_2 component	4.26	27.76	4.40	24.72
	N_2 component	20.45	–	18.30	–
	Mixture	3.50	–	5.27	–
$CH_4/CO_2/N_2$	CH_4 component	26.88	–[c]	26.42	–[c]
	CO_2 component	16.74	–[†]	14.50	–[†]
	N_2 component	57.04	–	58.87	–
	Mixture	10.67	–	11.31	–
Overall mean error		19.09	25.39	19.18	27.79
Overall increased performance		–	–	−0.47	−9.45

94 experimental data points

[a] Std MPTA mean pure fit error refers to the mean absolute deviation between experimentally measured excess adsorptions and those computed by (3) using (2) and (1)

[b] New MPTA mean pure fit error refers to the mean absolute deviation between experimentally measured excess adsorptions and those computed by (3) using (2) and (8) with individual z^i_0, ϵ^i_0 and β^i parameters

[c] Error on selectivity over 100% due to large error on the least adsorbed component

interaction with CH_4, which one has higher polarizability than N_2. The material was regenerated between each measurement under vacuum at 250 °C for 6 h. The measurements were performed volumetrically at 303 K and 323 K over a pressure ranging from 105 to 705 kPa. Overall, the new model overestimates the mixture adsorption by 5.95%, while the pure isotherms are underestimated by 2.62%.

Table 12 gives the mean error between the prediction of both approaches.

Another binary mixture adsorption experiment was carried out using the Zeolite-13X. This time, CO_2 and N_2 are considered on Zeolite-13X (Zeochem Co.) [11], which has a microporous volume of 0.21 cm^3/g and a BET surface of 164.3 m^2/g [35]. The adsorbent was regenerated between each new isotherm measurement under vacuum at 400 °C for 4 h. The measurements were performed volumetrically at 298 K and 318 K over a pressure ranging from 115 to 1020 kPa. Overall, the new model underestimates the mixture adsorption by 16.65%, while the pure isotherms are underestimated by 0.57%.

Table 13 gives the mean error between the prediction of both approaches.

3.10 Zeolite-ZSM-5

Binary mixtures of CO_2 and N_2 are considered on Zeolite-ZSM-5 (Zeochem Co.) [11], which has a microporous volume of 0.155 cm^3/g and a BET surface from 264 to 312.4 m^2/g [36]. The adsorbent was regenerated between each new isotherm measurement under vacuum at 400 °C for 4 h. The measurements were performed volumetrically at 298 K and 318 K over a pressure ranging from 120 to 1010 kPa. Overall, the new model underestimates the mixture adsorption by 7.51%, while the pure isotherms are underestimated by 1.48%.

Table 14 gives the mean error between the prediction of both approaches.

3.11 Zeolite-NaX

Binary mixtures of CO_2 and CO are considered on Zeolite-NaX, which has a microporous volume of 0.283 cm^3/g and a BET surface of 685 m^2/g [12]. The measurements were performed volumetrically at 323 K and 373 K at a pressure of 100 kPa. Overall, the new model underestimates the mixture adsorption by 6.15%, while the pure isotherms are overestimated by 0.65%.

Table 15 gives the mean error between the prediction of both approaches.

3.12 Zeolite H-Mordenite

Binary and ternary mixtures adsorption of CO_2, H_2S, and C_3H_8 are studied on hydrogen mordenite (Norton Company) [13], which has a BET surface of 400 m^2/g [37]. The measurements were performed volumetrically at 303 K over a pressure ranging from 1 to 61 kPa. Overall, the new model underestimates the mixture adsorption by 23.88%, while the pure isotherms are overestimated by 0.59%.

Table 16 gives the mean error between the prediction of both approaches.

4 Discussion

Tables 17 and 18 synthesize all the results and presented them under different scope. First, Table 17 compares standard and new MPTA model's adsorption accuracy based on mixture order (pure, binary, ternary), and separates results for total mixture from results for mixture components. Surprisingly, standard MPTA performs slightly better than

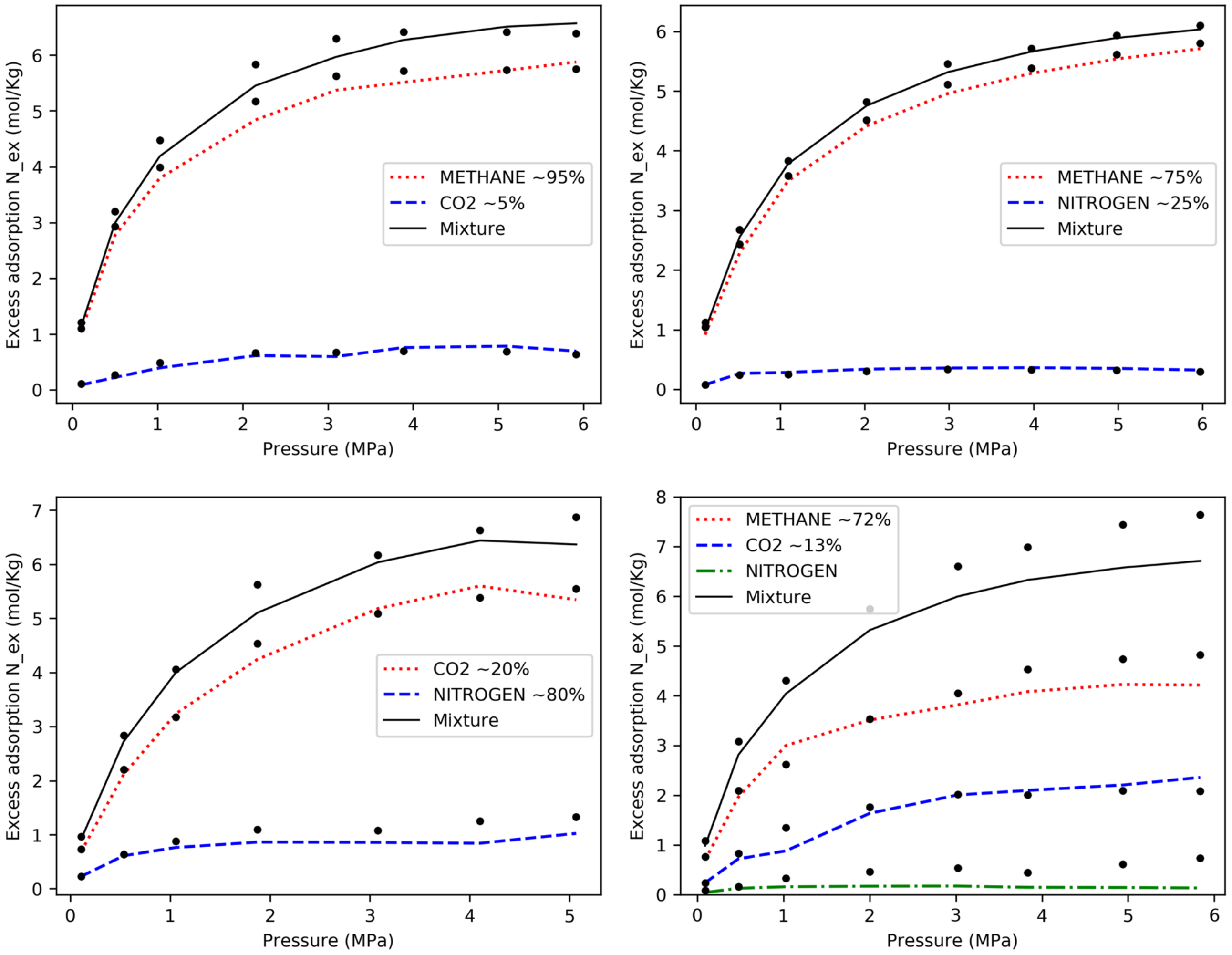

Fig. 4 New MPTA model selected examples of binary and ternary mixtures on Norit-R1 at 298 K and pressure up to 6 MPa

new MPTA for total binary mixture adsorption predictions. For all the cases except the total binary mixture, the new MPTA model performs better than the standard one, so globally, the new MPTA model is still the more accurate model. Moreover, even if the new MPTA model is slightly less accurate than standard MPTA for total binary mixture adsorption, both models are fairly accurate with around 6% accuracy.

Table 18 compares the binary mixture adsorption prediction accuracy of both models in the scope of adsorbent materials type. Here again, surprisingly, the standard MPTA model performs better than the new one for activated carbon total mixture adsorption. However, the new MPTA model still performs better for MOF, zeolite, and activated carbon component predictions. MOF is the adsorbent material with the best increases of performance with the new MPTA model (not a lot of data, however).

For all practical purposes, the most relevant information for gas mixture adsorption is the individual component adsorbed quantities rather than total mixture adsorption.

Table 5 Comparison of standard and new MPTA models on activated carbon AP3-60 at 298 K and pressure up to 10.8 MPa

System		Mean error (%)			
		Std MPTA[a]		New MPTA[b]	
		N_{ex}^i	Select	N_{ex}^i	Select
CO_2/N_2	CO_2 component	4.47	–	2.40	–
	N_2 component	33.45	62.57	27.91	52.62
	Mixture	2.60	–	2.64	–
CO_2/H_2	CO_2 component	3.38	–	4.00	–
	H_2 component	115.36	–[c]	108.44	–[c]
	Mixture	13.30	–	12.47	–
Overall mean error		34.10	62.57	31.68	52.62
Overall increased performance		–	–	7.10	15.90

40 experimental data points

[a] Std MPTA mean pure fit error refers to the mean absolute deviation between experimentally measured excess adsorptions and those computed by (3) using (2) and (1)

[b] New MPTA mean pure fit error refers to the mean absolute deviation between experimentally measured excess adsorptions and those computed by (3) using (2) and (8) with individual z_0^i, ϵ_0^i and β^i parameters

[c] Error on selectivity over 100% due to large error on the least adsorbed component

Table 6 Comparison of standard and new MPTA models on activated carbon BPL at 297 K and 301.4 K and pressure up to 2.5 MPa

System		Mean error (%)			
		Std MPTA[a]		New MPTA[b]	
		N_{ex}^i	Select	N_{ex}^i	Select
CH_4/C_2H_6 297 K	CH_4 component	13.57	–	12.88	–
	C_2H_6 component	12.98	20.92	15.16	20.16
	Mixture	9.04	–	9.64	–
CH_4/C_2H_6 301.4K	CH_4 component	24.62	–	23.72	–
	C_2H_6 component	12.96	45.01	13.14	49.26
	Mixture	6.50	–	6.56	–
Overall mean error		13.43	34.30	13.62	36.33
Overall increased performance		–	–	– 1.41	–5.92

54 experimental data points

[a] Std MPTA mean pure fit error refers to the mean absolute deviation between experimentally measured excess adsorptions and those computed by (3) using (2) and (1)

[b] New MPTA mean pure fit error refers to the mean absolute deviation between experimentally measured excess adsorptions and those computed by (3) using (2) and (8) with individual z_0^i, ϵ_0^i and β^i parameters

Table 7 Comparison of standard and new MPTA models on MOF-5 at 297 K and pressure from 0 to 1510 kPa

System		Mean error (%)			
		Std MPTA[a]		New MPTA[b]	
		N_{ex}^i	Select	N_{ex}^i	Select
CH_4/CO_2	CH_4 component	23.59	–	17.86	–
	CO_2 component	7.25	39.64	6.67	29.06
	Mixture	5.56	–	4.10	–
CH_4/N_2	CH_4 component	3.96	12.76	3.87	3.96
	N_2 component	10.04	–	6.09	–
	Mixture	4.48	–	3.97	–
CO_2/N_2	CO_2 component	5.50	47.77	5.22	33.36
	N_2 component	32.83	–	25.90	–
	Mixture	7.75	–	7.26	–
$N_2/CH_4/CO_2$	N_2 component	28.99	–	20.32	–
	CH_4 component	22.21	10.78[c]	15.79	10.54[c]
	CO_2 component	16.36	38.71[c]	15.83	29.81[c]
	Mixture	13.44	–	10.58	–
$H_2/CH_4/CO_2$	H_2 component	7.28	–	17.09	–
	CH_4 component	18.77	14.16[c]	13.18	7.93[c]
	CO_2 component	25.64	33.70[c]	12.12	30.36[c]
	Mixture	21.20	–	9.07	–
$H_2/N_2/CO_2$	H_2 component	19.29	–	26.53	–
	N_2 component	16.72	15.13[c]	5.88	29.54[c]
	CO_2 component	19.64	37.71[c]	12.05	39.66[c]
	Mixture	13.64	–	8.52	–
Overall mean error		16.43	27.64	12.61	21.88
Overall increased performance		–	–	23.25	20.84

40 experimental data points.

[a] Std MPTA mean pure fit error refers to the mean absolute deviation between experimentally measured excess adsorptions and those computed by (3) using (2) and (1)

[b] New MPTA mean pure fit error refers to the mean absolute deviation between experimentally measured excess adsorptions and those computed by (3) using (2) and (8) with individual z_0^i, ϵ_0^i and β^i parameters

[c] Represent the adsorption selectivity of the component compared to the first component

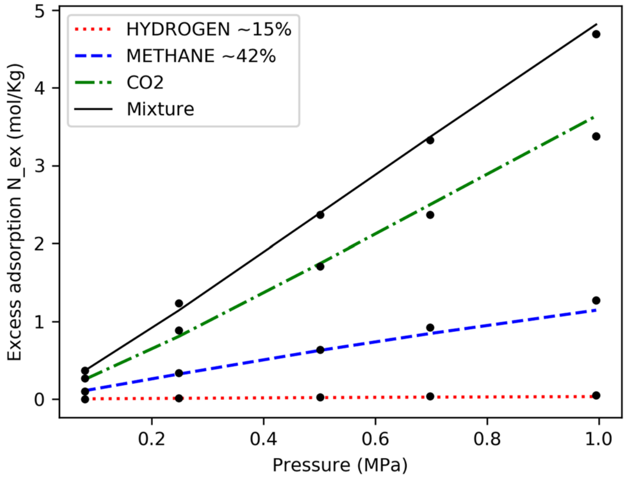

Fig. 5 New MPTA model selected examples of ternary mixture on MOF-5 at 297 K and pressure up to 1510 kPa

Table 8 Comparison of standard and new MPTA models on CuBTC at 297 K and pressure from 0 to 1 MPa

System		Mean error (%)			
		Std MPTA[a]		New MPTA[b]	
		N^i_{ex}	Select	N^i_{ex}	Select
$H_2/N_2/CO_2$	H_2 component	42.49	–	35.14	–
	N_2 component	22.08	38.92[c]	28.66	11.80[c]
	CO_2 component	3.93	83.67[c]	4.18	63.18[c]
	Mixture	2.90	–	2.10	–
Overall mean error		17.85	61.30	17.52	37.49
Overall increased performance		–	–	1.85	38.84

Three experimental data points.

[a] Std MPTA mean pure fit error refers to the mean absolute deviation between experimentally measured excess adsorptions and those computed by (3) using (2) and (1)

[b] New MPTA mean pure fit error refers to the mean absolute deviation between experimentally measured excess adsorptions and those computed by (3) using (2) and (8) with individual z^i_0, ϵ^i_0 and β^i parameters

[c] Represent the adsorption selectivity of the component compared to the first component

Table 9 Comparison of standard and new MPTA models on 4A-Zeolite at 423 K and 473 K and pressure close to 100 kPa

System		Mean error (%)			
		Std MPTA[a]		New MPTA[b]	
		N^i_{ex}	Select	N^i_{ex}	Select
C_3H_8/C_3H_6 423K	C_3H_8 component	18.65	–	18.46	–
	C_3H_6 component	4.03	32.26	3.80	30.59
	Mixture	2.89	–	2.94	–
C_3H_8/C_3H_6 473K	C_3H_8 component	14.72	–	13.56	–
	C_3H_6 component	2.64	15.80	5.86	12.15
	Mixture	3.76	–	3.40	–
Overall mean error		7.84	24.66	8.03	22.08
Overall increased performance		–	–	-2.42	10.46

13 experimental data points

[a] Std MPTA mean pure fit error refers to the mean absolute deviation between experimentally measured excess adsorptions and those computed by (3) using (2) and (1)

[b] New MPTA mean pure fit error refers to the mean absolute deviation between experimentally measured excess adsorptions and those computed by (3) using (2) and (8) with individual z^i_0, ϵ^i_0 and β^i parameters

The new MPTA model performs better than the standard ones for both binary and ternary components adsorption with an average accuracy of 15.77% and 34.46%, respectively.

Tables 19 and 20 give a comparison for the fitting parameter between the new and standard MPTA model for N_2/CO_2 and CH_4/N_2 mixture on activated carbon, MOF, and zeolite. In both cases, the standard MPTA parameters are largely dominated by the most adsorbed component (CO_2 and CH_4, respectively). Consequently, the ε_0 parameters of the least absorbed component differ substantially from the new MPTA model, where the components are individually fitted.

Table 10 Comparison of standard and new MPTA models on 5A-Zeolite at 296 K and pressure from 23 to 921 kPa

System		Mean error (%)			
		Std MPTA[a]		New MPTA[b]	
		N^i_{ex}	Select	N^i_{ex}	Select
O_2/N_2 open system	O_2 component	24.41	–	21.51	–
	N_2 component	4.48	40.41	2.89	33.28
	Mixture	2.39	–	1.62	–
O_2/N_2 closed system	O_2 component	17.98	–	14.69	–
	N_2 component	13.70	36.10	10.56	26.00
	Mixture	11.98	–	9.27	–
Overall mean error		11.61	39.18	9.48	31.20
Overall increased performance		–	–	18.3	20.3

21 experimental data points

[a] Std MPTA mean pure fit error refers to the mean absolute deviation between experimentally measured excess adsorptions and those computed by (3) using (2) and (1)

[b] New MPTA mean pure fit error refers to the mean absolute deviation between experimentally measured excess adsorptions and those computed by (3) using (2) and (8) with individual z^i_0, ϵ^i_0 and β^i parameters

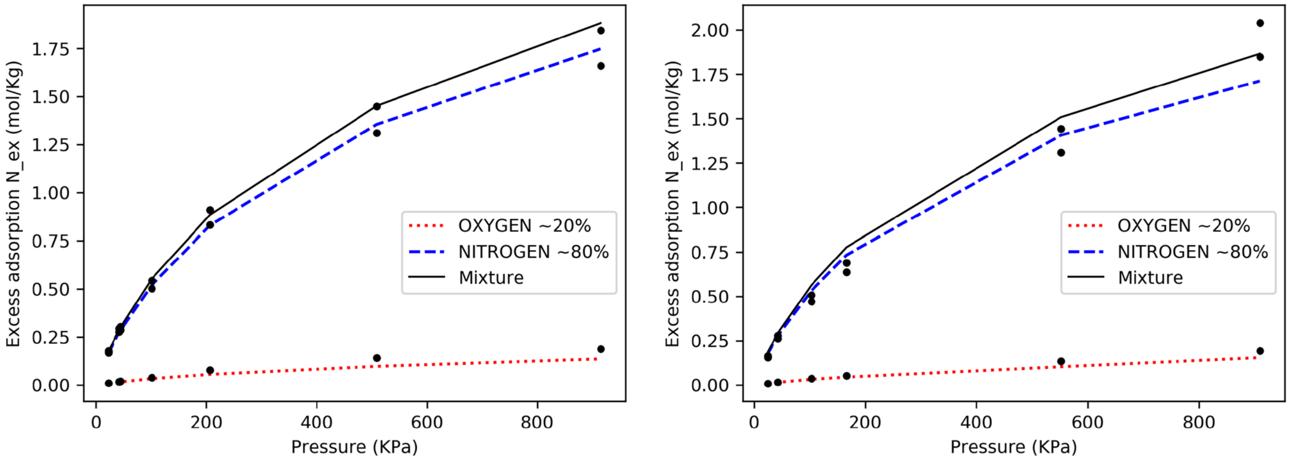

Fig. 6 Chosen examples of the new MPTA model for binary mixtures on Zeolite-5A at 296 K and pressure up to 921 kPa

Table 11 Comparison of standard and new MPTA models on Zeolite-5A at 303 K and 323 K, and pressure from 98 to 916 kPa

System		Mean error (%)			
		Std MPTA[a]		New MPTA[b]	
		N^{i}_{ex}	Select	N^{i}_{ex}	Select
CH_4/N_2 303 K	CH_4 component	6.00	–	9.32	–
	N_2 component	6.57	6.22	5.21	13.61
	Mixture	5.86	–	5.81	–
CH_4/N_2 323 K	CH_4 component	4.11	–	3.97	–
	N_2 component	5.12	4.24	8.37	9.58
	Mixture	3.99	–	3.77	–
Overall mean error		5.61	5.61	6.35	12.37
Overall increased performance		–	–	-13.19	-120.50

26 experimental data points

[a] Std MPTA mean pure fit error refers to the mean absolute deviation between experimentally measured excess adsorptions and those computed by (3) using (2) and (1)

[b] New MPTA mean pure fit error refers to the mean absolute deviation between experimentally measured excess adsorptions and those computed by (3) using (2) and (8) with individual z^{i}_{0}, ϵ^{i}_{0} and β^{i} parameters

Table 12 Comparison of standard and new MPTA models on Zeolite-13X at 303 K and 323 K, and pressure up to 700 kPa

System		Mean error (%)			
		Std MPTA[a]		New MPTA[b]	
		N^{i}_{ex}	Select	N^{i}_{ex}	Select
CH_4/N_2 303 K	CH_4 component	7.87	–	7.99	–
	N_2 component	6.06	14.31	3.37	9.52
	Mixture	6.20	–	6.20	–
CH_4/N_2 323 K	CH_4 component	13.11	–	8.68	–
	N_2 component	5.30	17.39	5.64	10.32
	Mixture	9.45	–	8.89	–
Overall mean error		7.88	15.71	6.71	9.88
Overall increased performance		–	–	14.85	37.11

33 experimental data points

[a] Std MPTA mean pure fit error refers to the mean absolute deviation between experimentally measured excess adsorptions and those computed by (3) using (2) and (1)

[b] New MPTA mean pure fit error refers to the mean absolute deviation between experimentally measured excess adsorptions and those computed by (3) using (2) and (8) with individual z^{i}_{0}, ϵ^{i}_{0} and β^{i} parameters

Table 13 Comparison of standard and new MPTA models on Zeolite-13X at 298 K and 318 K, and pressure up to 1 MPa

System		Mean error (%)			
		Std MPTA[a]		New MPTA[b]	
		N^{i}_{ex}	Select	N^{i}_{ex}	Select
CO_2/N_2 298 K	CO_2 component	5.93	–	4.56	–
	N_2 component	58.20	–[†]	53.12	–[†]
	Mixture	3.35	–	2.24	–
CO_2/N_2 318 K	CO_2 component	6.46	–	6.07	–
	N_2 component	59.97	–[c]	49.07	–[c]
	Mixture	4.15	–	4.16	–
Overall mean error		22.96	–	19.88	–
Overall increased performance		–	–	13.41	–

11 experimental data points.

[a] Std MPTA mean pure fit error refers to the mean absolute deviation between experimentally measured excess adsorptions and those computed by (3) using (2) and (1)

[b] New MPTA mean pure fit error refers to the mean absolute deviation between experimentally measured excess adsorptions and those computed by (3) using (2) and (8) with individual z^{i}_{0}, ϵ^{i}_{0} and β^{i} parameters

[c] Error on selectivity over 100% due to large error on the least adsorbed component

Table 14 Comparison of standard and new MPTA models on Zeolite-ZSM-5 at 298 K and 318 K, and pressure up to 1 MPa

System		Mean error (%)			
		Std MPTA[a]		New MPTA[b]	
		N^{i}_{ex}	Select	N^{i}_{ex}	Select
CO_2/N_2 298 K	CO_2 component	2.08	–	2.36	–
	N_2 component	44.80	106.17	26.40	43.91
	Mixture	2.09	–	1.21	–
CO_2/N_2 318 K	CO_2 component	2.27	–	2.00	–
	N_2 component	28.35	50.85	19.79	26.24
	Mixture	3.24	–	2.23	–
Overall mean error		13.48	74.90	8.87	33.92
Overall increased performance		–	–	34.20	54.71

23 experimental data points

[a] Std MPTA mean pure fit error refers to the mean absolute deviation between experimentally measured excess adsorptions and those computed by (3) using (2) and (1)

[b] New MPTA mean pure fit error refers to the mean absolute deviation between experimentally measured excess adsorptions and those computed by (3) using (2) and (8) with individual z^{i}_{0}, ϵ^{i}_{0} and β^{i} parameters

Table 15 Comparison of standard and new MPTA models on Zeolite-NaX at 323 K and 373 K under 1 Bar

System		Mean error (%)			
		Std MPTA[a]		New MPTA[b]	
		N^i_{ex}	Select	N^i_{ex}	Select
CO_2/CO 323 K	CO_2 component	22.33	43.22	24.51	36.82
	CO component	26.22	–	19.47	–
	Mixture	24.62	–	21.52	–
CO_2/CO 373K	CO_2 component	19.13	33.52	19.66	33.63
	CO component	22.04	–	22.06	–
	Mixture	16.39	–	16.80	–
Overall mean error		21.59	36.75	20.28	34.69
Overall increased performance		–	–	6.07	5.61

Three experimental data points

[a] Std MPTA mean pure fit error refers to the mean absolute deviation between experimentally measured excess adsorptions and those computed by (3) using (2) and (1)

[b] New MPTA mean pure fit error refers to the mean absolute deviation between experimentally measured excess adsorptions and those computed by (3) using (2) and (8) with individual z^i_0, ϵ^i_0 and β^i parameters

Table 16 Comparison of standard and new MPTA models on H-Mordenite at 303 K and pressure from 1 to 61 kPa

System		Mean error (%)			
		Std MPTA[a]		New MPTA[b]	
		N^i_{ex}	Select	N^i_{ex}	Select
CO_2/H_2S	CO_2 component	36.12	–	51.08	–
	H_2S component	7.33	72.78	10.37	145.12
	Mixture	6.32	–	2.20	–
C_3H_8/CO_2	C_3H_8 component	22.62	100.45	16.70	84.50
	CO_2 component	49.83	–	47.31	–
	Mixture	16.85	–	21.76	–
C_3H_8/H_2S	C_3H_8 component	47.15	–	45.10	–
	H_2S component	17.42	–[c]	15.93	–[c]
	Mixture	20.42	–	20.12	–
$CO_2/H_2S/C_3H_8$	CO_2 component	50.59	–	63.64	–
	H_2S component	92.01	–[c]	100.81	–[c]
	C_3H_8 component	82.49	–[c]	83.15	–[c]
	Mixture	29.42	–	31.45	–
Overall mean error		37.94	86.62	40.55	114.81
Overall increased performance		–	–	−6.88	−32.54

36 experimental data points.

[a] Std MPTA mean pure fit error refers to the mean absolute deviation between experimentally measured excess adsorptions and those computed by (3) using (2) and (1)

[b] New MPTA mean pure fit error refers to the mean absolute deviation between experimentally measured excess adsorptions and those computed by (3) using (2) and (8) with individual z^i_0, ϵ^i_0 and β^i parameters

[c] Error on selectivity over 100% due to large error on the least adsorbed component

Table 17 MPTA adsorption accuracy for pure gases, binary, and ternary mixtures

	Data	Std MPTA[a]	New MPTA[b]	Performance increase
Pure gases fit	877	4.71%	2.38%	49.5%
Total binary mixture	438	5.79%	5.93%	-2.4%
Binary components	876	17.01%	15.77%	7.3%
Total ternary mixture	72	14.45%	13.32%	7.8%
Ternary components	216	34.94%	34.46%	1.4%
	2479	12.16%	10.85%	10.8%

[a] Std MPTA mean pure fit error refers to the mean absolute deviation between experimentally measured excess adsorptions and those computed by (3) using (2) and (1)

[b] New MPTA mean pure fit error refers to the mean absolute deviation between experimentally measured excess adsorptions and those computed by (3) using (2) and (8) with individual z_0^i, ε_0^i and β^i parameters

Table 18 MPTA adsorption accuracy for binary prediction breakdown by adsorbent species

	Data	Std MPTA[a]	New MPTA[b]	Performance increase
AC total mixture	264	5.12%	5.67%	-9.7%
AC components	528	17.79%	16.86%	5.2%
MOF total mixture	18	5.99%	5.12%	14.5%
MOF components	36	14.33%	11.34%	20.9%
Zeolite total mixture	156	6.89%	6.46%	6.2%
Zeolite components	312	16.01%	14.44%	9.8%
	1314	13.27%	12.49%	5.9%

[a] Std MPTA mean pure fit error refers to the mean absolute deviation between experimentally measured excess adsorptions and those computed by (3) using (2) and (1)

[b] New MPTA mean pure fit error refers to the mean absolute deviation between experimentally measured excess adsorptions and those computed by (3) using (2) and (8) with individual z_0^i, ϵ_0^i and β^i parameters

Table 19 Comparison of the fitting parameters for N_2/CO_2 mixture on AC, MOF, and zeolite

Model	Gas	Parameter	AC F-400	MOF-5	Zeolite ZSM-5
New MPTA[b]	N_2	z_0^i (cm^3/g)	0.245	1.13	0.125
		ε_0^i (J/mol)	7289	2744	7310
		β^i	2.32	1.39	2.10
	CO_2	z_0^i (cm^3/g)	0.306	2.76	0.09
		ε_0^i (J/mol)	7637	1945	11568
		β^i	1.86	1.00	2.42
Std MPTA[a]	N_2/CO_2	z_0 (cm^3/g)	0.307	1.75	0.09
		$\varepsilon_0^{N_2}$ (J/mol)	5929	1893	8525
		$\varepsilon_0^{CO_2}$ (J/mol)	7768	2826	11585
		β	1.70	1.25	2.44
T		(K)	318.2	297	318
BET		(m^2/g)	850	3054	288
micro-volume		(cm^3/g)	0.495	1.31	0.155

[a] Std MPTA mean pure fit error refers to the mean absolute deviation between experimentally measured excess adsorptions and those computed by (3) using (2) and (1)

[b] New MPTA mean pure fit error refers to the mean absolute deviation between experimentally measured excess adsorptions and those computed by (3) using (2) and (8) with individual z_0^i, ε_0^i and β^i parameters

Table 20 Comparison of the fitting parameters for CH_4/N_2 mixture on AC, MOF, and zeolite

Model	Gas	Parameter	AC Norit-R1	MOF-5	Zeolite 13X
New MPTA[b]	CH_4	z_0^i (cm^3/g)	0.385	1.29	0.245
		ε_0^i (J/mol)	8095	3511	8479
		β^i	1.94	1.44	2.90
	N_2	z_0^i (cm^3/g)	0.311	1.13	3.74
		ε_0^i (J/mol)	7273	2744	573
		β^i	2.31	1.39	0.58
Std MPTA[a]	CH_4/N_2	z_0 (cm^3/g)	0.386	1.25	0.26
		$\varepsilon_0^{CH_4}$ (J/mol)	8085	3580	8238
		$\varepsilon_0^{N_2}$ (J/mol)	6141	2558	7223
		β	1.88	1.45	2.68
T		(K)	297	297	303
BET		(m^2/g)	1407	3054	164
micro-volume		(cm^3/g)	0.351	1.31	0.21

[a] Std MPTA mean pure fit error refers to the mean absolute deviation between experimentally measured excess adsorptions and those computed by (3) using (2) and (1)

[b] New MPTA mean pure fit error refers to the mean absolute deviation between experimentally measured excess adsorptions and those computed by (3) using (2) and (8) with individual z_0^i, ϵ_0^i and β^i parameters

5 Conclusion

A new approach to the Multicomponent Potential Theory of Adsorption was presented in which individual fitting parameters replaced the commons ones. Specifically, the new approach uses distinct values of the parameters z_0 (the limiting microporous volume) and β (the heterogeneity parameter) for the model pure gases fits. In the standard MPTA model, those parameters are shared by all the pure gases, which generated the coupling of pure gases. In this new formulation, there are individual parameters for each pure gases considered. This implies more fitting parameters ($3M$ parameters instead of M+2) but is nevertheless easier to understand and adjust because the model decomposed into M individual three parameters fit. The objective pursued is the ability to predict mixture adsorption without any experimental measurements by extrapolating parameters from one adsorbent to another. Under that scope, the independence of the components is a crucial step.

After testing over 500 experimental mixture data, the new approach performed 4.67% better than the usual model, which gives a mean error of 6.97% for total mixture excess adsorption, and an overall mean error of 15.30% if the component and total mixture adsorption are combined.

The best performance of the new MPTA model on binary mixture was achieved on MOF with a combined accuracy (component plus total mixture accuracy) of 9.27%, followed by Zeolite with an 11.78% accuracy, and finally activated carbon with an accuracy of 13.13%.

For the vast majority of cases, the new MPTA approach gives a better accuracy compared to the standard MPTA model. The only situations where standard MPTA performs better than the new model are for activated carbon total mixture adsorption and total binary mixture adsorption. However, the new MPTA model does perform better for activated carbon component adsorption and binary mixture component adsorption. As mention earlier, the most relevant prediction for multicomponent adsorption is the individual component adsorption. Overall, the component adsorption predictions of the new MPTA model are more accurate than the standard MPTA model, which justifies using the new MPTA model described in this paper.

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Compliance with ethical standards

Conflict of interest The authors declare that they have no conflict of interest.

References

1. Sudibandriyo M, Pan Z, Fitzgerald JE, Robinson RL, Gasem KA (2003) Adsorption of methane, nitrogen, carbon dioxide, and their binary mixtures on dry activated carbon at 318.2 K and pressures up to 13.6 MPa. Langmuir 19(13):5323. https://doi.org/10.1021/la020976k
2. Dreisbach F, Staudt R, Keller JU (1999) High pressure adsorption data of methane, nitrogen, carbon dioxide and their binary and ternary mixtures on activated carbon. Adsorption 5(3):215. https://doi.org/10.1023/A:1008914703884
3. Schell J, Casas N, Pini R, Mazzotti M (2012) Pure and binary adsorption of CO2, H2, and N2 on activated carbon. Adsorption 18(1):49. https://doi.org/10.1007/s10450-011-9382-y
4. He Y, Yun JH, Seaton NA (2004) Adsorption equilibrium of binary methane/ethane mixtures in BPL activated carbon: isotherms and calorimetric heats of adsorption. Langmuir 20(16):6668
5. Kloutse F, Hourri A, Natarajan S, Benard P, Chahine R (2018) Experimental benchmark data of CH4, CO2 and N2 binary and ternary mixtures adsorption on MOF-5. Sep Purif Technol 197:228. https://doi.org/10.1016/j.seppur.2018.01.013
6. Kloutse F, Hourri A, Natarajan S, Benard P, Chahine R (2018) Hydrogen separation by adsorption: experiments and modelling of H2–N2–CO2 and H2–CH4–CO2 mixtures adsorption on CuBTC and MOF-5. Microporous Mesoporous Mater 271:175
7. Grande CA, Gigola C, Rodrigues AE (2003) Propane–propylene binary adsorption on zeolite 4A. Adsorption 9(4):321
8. Talu O, Li J, Kumar R, Mathias PM, Moyer JD Jr, Schork JM (1996) Measurement and analysis of oxygen/nitrogen/5A-zeolite adsorption equilibria for air separation. Gas Sep Purif 10(3):149
9. Bakhtyari A, Mofarahi M (2014) Pure and binary adsorption equilibria of methane and nitrogen on zeolite 5A. J Chem Eng Data 59(3):626
10. Mofarahi M, Bakhtyari A (2015) Experimental investigation and thermodynamic modeling of CH4/N2 adsorption on zeolite 13X. J Chem Eng Data 60(3):683
11. Hefti M, Marx D, Joss L, Mazzotti M (2015) Adsorption equilibrium of binary mixtures of carbon dioxide and nitrogen on zeolites ZSM-5 and 13X. Microporous Mesoporous Mater 215:215
12. Belmabkhout Y, Pirngruber G, Jolimaitre E, Methivier A (2007) A complete experimental approach for synthesis gas separation studies using static gravimetric and column breakthrough experiments. Adsorption 13(3–4):341
13. Talu O, Zwiebel I (1986) Multicomponent adsorption equilibria of nonideal mixtures. AIChE J 32(8):1263
14. Shapiro AA, Stenby EH (1998) Potential theory of multicomponent adsorption. J Colloid Interface Sci 201(2):146. https://doi.org/10.1006/jcis.1998.5424
15. Polanyi M (1963) The potential theory of adsorption. Science 141(3585):1010. https://doi.org/10.1126/science.141.3585.1010
16. Monsalvo M, Shapiro A (2007) Modeling adsorption of binary and ternary mixtures on microporous media. Fluid Phase Equilibria 254(1–2):91. https://doi.org/10.1016/j.fluid.2007.02.006
17. Monsalvo M, Shapiro A (2007) Prediction of adsorption from liquid mixtures in microporous media by the potential theory. Fluid Phase Equilibria 261(1–2):292. https://doi.org/10.1016/j.fluid.2007.07.067

18. Monsalvo MA, Shapiro AA (2009) Modeling adsorption of liquid mixtures on porous materials. J Colloid Interface Sci 333(1):310
19. Dubinin MM (1989) Fundamentals of the theory of adsorption in micropores of carbon adsorbents: characteristics of their adsorption properties and microporous structures. Pure Appl Chem 61(11):1841. https://doi.org/10.1351/pac198961111841
20. Dundar E, Zacharia R, Chahine R, Bénard P (2014) Potential theory for prediction of high-pressure gas mixture adsorption on activated carbon and MOFs. Sep Purif Technol 135:229. https://doi.org/10.1016/j.seppur.2014.08.021
21. Dundar E, Zacharia R, Chahine R, Bénard P (2014) Performance comparison of adsorption isotherm models for supercritical hydrogen sorption on MOFs. Fluid Phase Equilibria 363:74. https://doi.org/10.1016/j.fluid.2013.11.029
22. Stoeckli F (1998) Recent developments in Dubinin's theory. Carbon 36(4):363
23. Terzyk AP, Gauden PA, Kowalczyk P (2002) What kind of pore size distribution is assumed in the Dubinin–Astakhov adsorption isotherm equation? Carbon 40(15):2879
24. Gervais Lavoie R, Ouellet M, Hamelin J, Bénard P (2018) Numerical implementation of the multicomponent potential theory of adsorption in Python using the NIST Refprop database. Commun Comput Phys 23(5):1602. https://doi.org/10.4208/cicp.OA-2017-0012arXiv:1702.05401
25. Myers A (2002) Thermodynamics of adsorption in porous materials. AIChE J 48(1):145. https://doi.org/10.1002/aic.690480115
26. Lemmon E, Huber M, McLinden M (2013) NIST standard reference database 23: reference fluid thermodynamic and transport properties-REFPROP, version 9.1. National Institute of Standards and Technology, Standard Reference Data Program, Gaithersburg
27. Newville M, Stensitzki T, Allen DB, Rawlik M, Ingargiola A, Nelson A (2016) LMFIT: non-linear least-square minimization and curve-fitting for Python. Astrophysics Source Code Library
28. Naseri AA, Dehghani MR, Behzadi B (2014) Modeling adsorption in binary associating solvents using the extended MPTA model. Adsorption 20(4):555
29. Bjørner MG, Shapiro AA, Kontogeorgis GM (2013) Potential theory of adsorption for associating mixtures: possibilities and limitations. Ind Eng Chem Res 52(7):2672. https://doi.org/10.1021/ie302144t
30. Bartholdy S, Bjørner MG, Solbraa E, Shapiro A, Kontogeorgis GM (2013) Capabilities and limitations of predictive engineering theories for multicomponent adsorption. Ind Eng Chem Res 52(33):11552
31. Nesterov I, Shapiro A, Kontogeorgis GM (2015) Multicomponent adsorption model for polar and associating mixtures. Ind Eng Chem Res 54(11):3039
32. Russell BP, Levan MD (1994) Pore size distribution of BPL activated carbon determined by different methods. Carbon 32(5):845
33. Sowunmi AR, Folayan CO, Anafi FO, Ajayi OA, Omisanya NO, Obada DO, Dodoo-Arhin D (2018) Dataset on the comparison of synthesized and commercial zeolites for potential solar adsorption refrigerating system. Data Br 20:90–95
34. Li Y, Guan HM, Chung TS, Kulprathipanja S (2006) Effects of novel silane modification of zeolite surface on polymer chain rigidification and partial pore blockage in polyethersulfone (PES)-zeolite A mixed matrix membranes. J Membr Sci 275(1–2):17
35. Zhang Z, Zhang W, Chen X, Xia Q, Li Z (2010) Adsorption of CO2 on zeolite 13X and activated carbon with higher surface area. Sep Sci Technol 45(5):710
36. Sang S, Chang F, Liu Z, He C, He Y, Xu L (2004) Difference of ZSM-5 zeolites synthesized with various templates. Catal Today 93:729
37. Sagert N, Pouteau R, Bailey M, Sargent F (1972) Benzene radical cation formation on hydrogen mordenite. The role of adsorbed oxygen. Can J Chem 50(13):2041