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 CH₄, CO₂, N₂, H₂, O₂, H₂S, C₂H₆, C₃H₆, and C₃H₈ 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 CH₄, CO₂, N₂, H₂, O₂, H₂S, C₂H₆, C₃H₆, and C₃H₈. 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
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 $\epsilon$, generated by the surface [17, 18]. A common choice for this purpose is the Dubinin–Radushkevich–Astakhov [19–21] potential (DRA), given by

$$\epsilon(z) = \begin{cases} \epsilon_0 \left( \ln \frac{z}{z_0} \right)^{1/\beta} & \text{if } 0 \leq z \leq z_0, \\ 0 & \text{if } z > z_0, \end{cases}$$

where $\epsilon_0$ and $z_0$ are the characteristic energy of adsorption and the limiting micropore volume, respectively. $\beta$ is a parameter which is usually interpreted as a quantification of the heterogeneity of the adsorbent [22, 23]. Usually, for activated carbon, the parameter $\beta$ is set to 2, while $\epsilon_0$ 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 $\epsilon(z)$.

The MPTA model is defined by [14, 25]

$$\mu_B(T, \rho_B) = \mu_{Ad}(T, \rho_{Ad}) - \epsilon,$$

where $\mu_B$ and $\rho_B$ are, respectively, the chemical potentials and the fluid density in the bulk phase, while $\mu_{Ad}$ and $\rho_{Ad}$ 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 $z_0$, $\epsilon_0$ and $\beta$ through the potential $\epsilon$. Correspondence 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 $\rho_{Ad}(z)$ from the chemical potentials. The (Gibbs) excess adsorption $N_{ex}$ (which is what is experimentally measured) is then calculated from

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

Optimal values for the fittings parameters are obtained by minimizing the difference $N_{ex}(\rho_B) - N_{ex}^{ref}(\rho_B)$ 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

$$\epsilon_i(z) = \begin{cases} \epsilon_0^i \left( \ln \frac{z}{z_0} \right)^{1/\beta} & \text{if } 0 \leq z \leq z_0, \\ 0 & \text{if } z > z_0, \end{cases}$$

where $\epsilon_0^i$ refers to a given component. The parameters $z_0$ and $\beta$ are generally assumed to be common to all mixture components [28]. Equation (2) now becomes a non-linear coupled system of $M$ equations

$$\mu_{B}^{i}(\rho_B, x_B^{i}) + \epsilon_i(z) - \mu_{Ad}^{i}(\rho_{Ad}(z), x_{Ad}^{i}(z)) = 0, \quad i = 1 \ldots M,$$

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

$$N_{ex}^{i}(\rho_B) = \int_0^{z_0} \left( \rho_{Ad}(z) x_{Ad}^{i}(z) - \rho_B x_B^{i} \right) dz, \quad i = 1 \ldots M.$$
Finally, the total adsorbed amount is the sum of the contributions of each component

\[ N_{ex}(\rho_b) = \sum_{i=1}^{M} N_{ex}^i(\rho_b). \] (7)

A key feature of the MPTA model is that the fitting parameters \(\varepsilon_i\) and \(z_0\) (and possibly \(\beta\)) 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 \(\beta\) parameters

2.1 Conceptual justification of the new model

Using unique values of \(z_0\) and \(\beta\) 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 \(\beta\) 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 \(\varepsilon_{0 A}, \varepsilon_{0 B}, z_{0 A}, z_{0 B},\) and \(\beta\).
- Now, if a new mixture of gas A and C is considered, parameters \(\varepsilon_{0 A}, \varepsilon_{0 C}, z_{0 A}, z_{0 C},\) and \(\beta\) cannot be reused.
- The model must be refit using the new A and C isotherms to obtain \(\varepsilon_{0 C} A, \varepsilon_{0 C} B, z_{0 C} A, z_{0 C} B,\) and \(\beta\).

Since \(\varepsilon_i, z_i\) 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 \(\varepsilon\). 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 \(\varepsilon_0\) 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 \(\beta\) can be introduced from minor modifications of the fluid–surface potential which now reads

\[ \varepsilon^i(z) = \begin{cases} \varepsilon_0^i \left(\ln \frac{z_0^i}{z}\right)^{1/\beta_i} & \text{if } 0 \leq z \leq z_0^{i'}, \\ 0 & \text{if } z > z_0^{i'}. \end{cases} \] (8)

Now, \(\varepsilon_0^i, z_0^i,\) and \(\beta^i\) 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 $z_0 < z \leq z_j'$. In that region, the surface potential $\epsilon'(z) = 0$ since $z > z_0'$, 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 $\epsilon'(z) \neq 0$ as $z \leq z_0'$. However, the fact that the component $j$ is affected by the adsorbent will modify its local molar fraction $x_{Adj}(z)$. Since $\sum_j x_{Adj} = 1$, local molar fractions are not independent and then, $x_{Adi}$ 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 $z_0' < z \leq z_j'$ 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 $z_0' < z \leq z_j'$ (the light gray area), we see that the molar fraction of CH$_4$ vary with $z$ even if the surface potential $\epsilon^{CH_4}(z)$ vanish in that region. At $z = z_0'$, the CH$_4$ starts to interact with the surface through non-vanishing $\epsilon^{CH_4}(z)$, and we observe a change in the reads of the molar fraction. The sharp variation of the molar fraction at $z = z_0'$ is obviously not physical. It came from the DRA potential, which is not smooth at $z = z_0'$. 

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.

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 $z < z_j^{max}$. For $z \geq z_j^{max}$, the integral vanishes, and then, the excess (Gibbs) adsorption for each component is

$$N_{exi}(\rho_B) = \int_{z_0}^{z_j^{max}} (\rho_{Ad}(z)x_{Adi}(z) - \rho_Bx_i^0) dz, \quad i = 1 \ldots M \tag{9}$$

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

Remark that the indirectly–interacting region of a component (the region $z_0' < z \leq z_j'$ 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 $\rho_{Ad}(z)x_{Adi}(z) - \rho_Bx_i^0 < 0$ in the indirectly–interacting region. The behavior of the component $i$ in the region $z_0' < z \leq z_j'$ 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].
\[ S_{ij} = \frac{N_{ex}^i z_B^j}{N_{ex}^i z_B}, \quad (10) \]

### 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 \( z_0^i \) parameters. As discussed in the previous section, the implementation of those individual \( z_0^i \) 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 \((\epsilon^i_0, z_0^i, \text{ and } \beta)\) instead of \(M + 2\) parameters \((\epsilon^i_0, z_0, \text{ and } \beta)\) 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 \( \epsilon_i, z_0\) and \( \beta\) values have been found for a pure gas, there will be no need to refit the model on this gas. Those individual parameters encompass 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 \((\epsilon_i, z_0, \text{ and } \beta)\), 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 \( z_0^i \) 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 \( z_0^i \) 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 \( z_0^i \) 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 \( z_0^i \) 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 \( \beta\) parameter of the DRA potential is treated as an individually adjustable parameter when \( \beta\) 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 \( N_{ex}^\text{Tot} \) (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 \( \chi_{Ad}^i \) and corresponds to the average proportion of component \( i \) in the adsorbed phase. \( \chi_{Ad}^i \) is then calculated from the initial and equilibrium states, and the components adsorption are calculated from

\[ N_{ex}^i = N_{ex}^\text{Tot} \chi_{Ad}^i \quad (11) \]

The point here is that both \( N_{ex}^\text{Tot} \) and \( \chi_{Ad}^i \) are tainted by experimental uncertainties such that

\[ (\delta N_{ex}^i)^2 = (\delta N_{ex}^\text{Tot} \chi_{Ad}^i)^2 + (N_{ex}^i \delta \chi_{Ad}^i)^2 \quad (12) \]

Dividing both side by \( (N_{ex}^i)^2 \), we obtain the relative error propagation equation

\[ \left( \frac{\delta N_{ex}^i}{N_{ex}^i} \right)^2 = \left( \frac{\delta N_{ex}^\text{Tot} \chi_{Ad}^i}{N_{ex}^i \chi_{Ad}^i} \right)^2 + \left( \frac{\delta \chi_{Ad}^i}{N_{ex}^i \chi_{Ad}^i} \right)^2 \quad (13) \]

When considering a mixture of different component behavior, it is not uncommon to come across experimental conditions where \( N_{ex}^i \) is very small compared to \( N_{ex}^\text{Tot} \). Since \( \delta \chi_{Ad}^i \) 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 \( N_{ex}^\text{Tot} \sim 6.2 \text{ mmol/g} \) and \( \delta \chi_{Ad}^i \sim 0.002 \). In that particular case, \( N_{ex}^i \sim 0.02 \text{ mmol/g} \), and then, the last term of \((13)\) gives an unacceptable relative uncertainty of \( \sim 60\% \) on \( N_{ex}^i \). 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 \( N_{ex}^\text{Tot} \) and 1% on the smallest \( x_B^i \) 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”
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 \( N^i_{\text{ex}} \) 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 \( \text{CH}_4, \text{CO}_2, \text{N}_2 \), 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 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 | \( \text{CH}_4/\text{N}_2/\text{CO}_2 \) | 318.2 | 2.82%               | 1.91%             |
| AC Norit R1     | \( \text{CH}_4/\text{N}_2/\text{CO}_2 \) | 298  | 3.17%               | 2.12%             |
| AC AP3-60       | \( \text{N}_2/\text{CO}_2/\text{H}_2 \) | 298  | 2.63%               | 2.83%             |
| AC BPL [4]      | \( \text{CH}_4/\text{C}_2\text{H}_6 \) | 297, 301.4 | 5.03%               | 1.46%             |
| MOF-5 [5, 6]    | \( \text{CH}_4/\text{N}_2/\text{H}_2/\text{CO}_2 \) | 297  | 8.91%               | 3.60%             |
| CuBTC [6]       | \( \text{N}_2/\text{H}_2/\text{CO}_2 \) | 297  | 2.96%               | 2.45%             |
| Zeolite-4A [7]  | \( \text{C}_2\text{H}_4/\text{C}_2\text{H}_6 \) | 423/473 | 4.94%               | 2.40%             |
| Zeolite-5A [8]  | \( \text{O}_2/\text{N}_2 \) | 296  | 2.82%               | 1.31%             |
| Zeolite-5A [9]  | \( \text{CH}_4/\text{N}_2 \) | 303/323 | 6.14%               | 3.90%             |
| Zeolite-13X [10]| \( \text{CH}_4/\text{N}_2 \) | 303/323 | 7.04%               | 3.36%             |
| Zeolite-13X [11]| \( \text{CO}_2/\text{N}_2 \) | 298/318 | 3.07%               | 0.95%             |
| Zeolite-ZSM-5 [11]| \( \text{CO}_2/\text{N}_2 \) | 298/318 | 3.72%               | 2.63%             |
| Zeolite-NaX [12]| \( \text{CO}_2/\text{CO} \) | 323/373 | 5.46%               | 2.24%             |
| Zeolite H-Mordenite [13]| \( \text{CO}_2/\text{H}_2/\text{C}_2\text{H}_6 \) | 303  | 3.25%               | 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 \( z^i_0 \), \( \epsilon^i_0 \) and \( \beta \) parameters

### 3.2 AC Norit R1

Binary and ternary mixtures of \( \text{CH}_4, \text{N}_2, \text{CO}_2 \) 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 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 7.68%, while the pure isotherms are underestimated by 0.82%.
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$_2$H$_6$ 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$_3$H$_8$ and C$_3$H$_6$ 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.
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 MPTA¹ | New MPTA² |       |       |
|               | Nᵢₑₓ Select | Nᵢₑₓ Select |       |       |
| CH₄/CO₂       | CH₄ component | 36.88 – | 36.32 – |       |
|               | CO₂ component | 9.07   | 40.97 | 7.71  | 39.83 |
|               | Mixture       | 5.79   | –     | 5.66  | –     |
| CH₄/N₂        | CH₄ component | 7.86   | 8.93  | 12.02 | 16.89 |
|               | N₂ component  | 7.00   | –     | 6.13  | –     |
|               | Mixture       | 4.93   | –     | 5.36  | –     |
| CO₂/N₂        | CO₂ component | 4.26   | 27.76 | 4.40  | 24.72 |
|               | N₂ component  | 20.45  | –     | 18.30 | –     |
|               | Mixture       | 3.50   | –     | 5.27  | –     |
| CH₄/CO₂/N₂    | CH₄ component | 26.88 – | 26.42 – |       |
|               | CO₂ component | 16.74 – | 14.50 – |       |
|               | N₂ 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

¹ 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)

² 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 $z''_k$, $c''_k$ and $\beta$ parameters

³ Error on selectivity over 100% due to large error on the least adsorbed component

Another binary mixture adsorption experiment was carried out using the Zeolite-13X. This time, CO₂ and N₂ are considered on Zeolite-13X (Zeochem Co.) [11], which has a microporous volume of 0.155 cm³/g and a BET surface from 264 to 312.4 m²/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 115 to 1010 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 CO₂ and N₂ are considered on Zeolite-ZSM-5 (Zeochem Co.) [11], which has a microporous volume of 0.283 cm³/g and a BET surface from 264 to 312.4 m²/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 CO₂ and CO are considered on Zeolite-NaX, which has a microporous volume of 0.283 cm³/g and a BET surface from 264 to 312.4 m²/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 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 CO₂, H₂S, and C₃H₄ are studied on hydrogen mordenite (Norton Company) [13], which has a BET surface of 400 m²/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
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<sup>a</sup> | New MPTA<sup>b</sup> |
|-----------------|----------------|-----------------------|-----------------------|
|                 | N<sub>ex</sub> | Select                | N<sub>ex</sub> | Select |
| CO₂/N₂         | CO₂ component | 4.47 -                | 2.40 -                |        |
|                 | N₂ component  | 33.45 62.57 27.91 52.62 | 62.57 27.91 52.62 2.60 - | 2.64 - |
|                 | Mixture       | 13.30 -               | 12.47 -               |        |
| CO₂/H₂         | CO₂ component | 3.38 -                | 4.00 -                |        |
|                 | H₂ component  | 115.36 -              | 108.44 -              |        |
|                 | Mixture       | 34.10 62.57 31.68 52.62 | 62.57 31.68 52.62 7.10 - | 15.90 |
| Overall mean error | –             | –                     | –                     |        |
| Overall increased performance | –             | –                     | –                     | 7.10 - 15.90 |

40 experimental data points

<sup>a</sup> 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)

<sup>b</sup> 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 \( z_i^0, \kappa_i^0 \) and \( \beta_i \) parameters

<sup>c</sup> 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<sup>a</sup> | New MPTA<sup>b</sup> |
|-----------------|----------------|-----------------------|-----------------------|
|                 | N<sub>ex</sub> | Select                | N<sub>ex</sub> | Select |
| CH₄/CO₂         | CH₄ component | 13.57 -               | 12.88 -               |        |
|                 | CH₄ component | 12.98 20.92 15.16 20.16 | 20.92 15.16 20.16 9.04 - | 9.64 - |
|                 | Mixture       | 24.62 -               | 23.72 -               |        |
| CH₄/C₂H₆        | CH₄ component | 12.96 45.01 13.14 49.26 | 45.01 13.14 49.26 6.50 - | 6.56 - |
|                 | Mixture       | 13.43 34.30 13.62 36.33 | 34.30 13.62 36.33 1.41 - | -5.92 |
| Overall mean error | –             | –                     | –                     |        |
| Overall increased performance | –             | –                     | –                     | 1.41 - -5.92 |

54 experimental data points

<sup>a</sup> 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)

<sup>b</sup> 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 \( z_i^0, \kappa_i^0 \) and \( \beta_i \) parameters

<sup>c</sup> Represent the adsorption selectivity of the component compared to the first component

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<sup>a</sup> | New MPTA<sup>b</sup> |
|-----------------|----------------|-----------------------|-----------------------|
|                 | N<sub>ex</sub> | Select                | N<sub>ex</sub> | Select |
| CH₄/CO₂         | CH₄ component | 24.62 -               | 23.72 -               |        |
|                 | CH₄ component | 18.77 14.16 13.18 7.93c | 14.16 13.18 7.93c 25.64 - | 33.70 - |
|                 | Mixture       | 5.56 – 6.09 – 3.97 – | 6.09 – 3.97 – 3.97 – |
| CO₂/N₂         | CO₂ component | 5.50 47.77 5.22 33.36 | 47.77 5.22 33.36 7.75 – | 7.26 – |
|                 | N₂ component  | 32.83 – 25.90 – 23.59 – | 25.90 – 23.59 – 23.59 – |
|                 | Mixture       | 4.48 – 3.97 – 3.00 – | 3.97 – 3.00 – 3.00 – |
| Overall mean error | –             | –                     | –                     |        |
| Overall increased performance | –             | –                     | –                     | 7.10 - 15.90 |

40 experimental data points

<sup>a</sup> 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)

<sup>b</sup> 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 \( z_i^0, \kappa_i^0 \) and \( \beta_i \) parameters

<sup>c</sup> Represent the adsorption selectivity of the component compared to the first component
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 $\epsilon$ 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<sup>a</sup> | New MPTA<sup>b</sup> |
|-------------------------------|----------------|----------------------|----------------------|
|                               |               | N<sub>ex</sub> | Select | N<sub>ex</sub> | Select |
| O<sub>2</sub>/N<sub>2</sub> open system | O<sub>2</sub> component | 24.41 | – | 21.51 | – |
|                               | N<sub>2</sub> component | 4.48  | 40.41 | 2.89 | 33.28 |
|                               | Mixture       | 2.39  | –  | 1.62 | – |
| O<sub>2</sub>/N<sub>2</sub> closed system | O<sub>2</sub> component | 17.98 | – | 14.69 | – |
|                               | N<sub>2</sub> 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

<sup>a</sup> 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)

<sup>b</sup> 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 \( z_i^0, r_i^0 \) and \( \beta_i \) 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        | New MPTA |
|                 | N_ex Select | N_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    | 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, c_i^0 and beta_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        | New MPTA |
|                 | N_ex Select | N_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    | 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, c_i^0 and beta_i parameters

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

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        | New MPTA |
|                 | N_ex Select | N_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| 49.07| -    |       |
|                 | Mixture        | 4.15 | 4.16 | -    |       |
| Overall mean    | 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, c_i^0 and beta_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        | New MPTA |
|                 | N_ex Select | N_ex Select |
| CO_2/N_2 298 K | CO_2 component | 2.08 | 2.36 | -    |
|                 | N_2 component  | 44.80| 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| 19.79| 26.24|
|                 | Mixture        | 3.24 | 2.23 | -    |       |
| Overall mean    | 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, c_i^0 and beta_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<sup>a</sup> | New MPTA<sup>b</sup> |
|-------------------|----------------|-----------------------|-----------------------|
|                   | N<sub>ex</sub> | Select                | N<sub>ex</sub> | Select |
| CO<sub>2</sub>/CO | CO<sub>2</sub> component | 22.33 | 43.22 | 24.51 | 36.82 |
|                   | CO component   | 26.22 | –     | 19.47 | –     |
|                   | Mixture        | 24.62 | –     | 21.52 | –     |
| CO<sub>2</sub>/CO | CO<sub>2</sub> 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

<sup>a</sup> 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)

<sup>b</sup> 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 \( z_0', c_0' \) and \( \beta' \) 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<sup>a</sup> | New MPTA<sup>b</sup> |
|-------------------|----------------|-----------------------|-----------------------|
|                   | N<sub>ex</sub> | Select                | N<sub>ex</sub> | Select |
| CO<sub>2</sub>/H<sub>2</sub>S | CO<sub>2</sub> component | 36.12 | –     | 51.08 | –     |
|                   | H<sub>2</sub>S component | 7.33 | 72.78 | 10.37 | 145.12 |
|                   | Mixture        | 6.32 | –     | 2.20 | –     |
| C<sub>2</sub>H<sub>6</sub>/CO<sub>2</sub> | C<sub>2</sub>H<sub>6</sub> component | 22.62 | 100.45 | 16.70 | 84.50 |
|                   | CO<sub>2</sub> component | 49.83 | –     | 47.31 | –     |
|                   | Mixture        | 16.85 | –     | 21.76 | –     |
| C<sub>2</sub>H<sub>6</sub>/H<sub>2</sub>S | C<sub>2</sub>H<sub>6</sub> component | 47.15 | –     | 45.10 | –     |
|                   | H<sub>2</sub>S component | 17.42 | –<sup>c</sup> | 15.93 | –<sup>c</sup> |
|                   | Mixture        | 20.42 | –     | 20.12 | –     |
| CO<sub>2</sub>/H<sub>2</sub>S/C<sub>3</sub>H<sub>8</sub> | CO<sub>2</sub> component | 50.59 | –     | 63.64 | –     |
|                   | H<sub>2</sub>S component | 92.01 | –<sup>c</sup> | 100.81 | –<sup>c</sup> |
|                   | C<sub>3</sub>H<sub>8</sub> component | 82.49 | –<sup>c</sup> | 83.15 | –<sup>c</sup> |
|                   | 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.

<sup>a</sup> 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)

<sup>b</sup> 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 \( z_0', c_0' \) and \( \beta' \) parameters

<sup>c</sup> 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 | New MPTA | 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%                |

\[a\] 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 \(z_i^*, \epsilon_0^*, \) and \(\beta^*\) parameters

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

| Data                      | Std MPTA | New MPTA | 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%                |
| Zeolite components        | 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 \(z_i^*, \epsilon_0^*, \) and \(\beta^*\) parameters

Table 19 Comparison of the fitting parameters for \(\text{N}_2/\text{CO}_2\) mixture on AC, MOF, and zeolite

| Model            | Gas     | Parameter | AC F-400 | MOF-5 | Zeolite ZSM-5 |
|------------------|---------|-----------|----------|-------|---------------|
| New MPTA         | \(\text{N}_2\) | \(z_0^*\) (cm\(^3\)/g) | 0.245    | 1.13  | 0.125         |
|                  |         | \(\epsilon_0^*(\text{J/mol})\) | 7289     | 2744  | 7310          |
|                  |         | \(\beta^*\) | 2.32     | 1.39  | 2.10          |
|                  | \(\text{CO}_2\) | \(z_0^*\) (cm\(^3\)/g) | 0.306    | 2.76  | 0.99          |
|                  |         | \(\epsilon_0^*(\text{J/mol})\) | 7637     | 1945  | 11568         |
|                  |         | \(\beta^*\) | 1.86     | 1.00  | 2.42          |

| Std MPTA         | \(\text{N}_2/\text{CO}_2\) | \(z_0^*\) (cm\(^3\)/g) | 0.307    | 1.75  | 0.09          |
|                  |         | \(\epsilon_0^*(\text{J/mol})\) | 5929     | 1893  | 8525          |
|                  |         | \(\beta^*\) | 1.70     | 1.25  | 2.44          |

\[a\] 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 \(z_i^*, \epsilon_0^*, \) and \(\beta^*\) parameters

Table 20 Comparison of the fitting parameters for \(\text{CH}_4/\text{N}_2\) mixture on AC, MOF, and zeolite

| Model            | Gas     | Parameter | AC Norit-R1 | MOF-5 | Zeolite 13X |
|------------------|---------|-----------|-------------|-------|-------------|
| New MPTA         | \(\text{CH}_4\) | \(z_0^*\) (cm\(^3\)/g) | 0.385    | 1.29  | 0.245         |
|                  |         | \(\epsilon_0^*(\text{J/mol})\) | 8095     | 3511  | 8479         |
|                  |         | \(\beta^*\) | 1.94      | 1.44  | 2.90         |
|                  | \(\text{N}_2\) | \(z_0^*\) (cm\(^3\)/g) | 0.311    | 1.33  | 3.74         |
|                  |         | \(\epsilon_0^*(\text{J/mol})\) | 7273     | 2744  | 573          |
|                  |         | \(\beta^*\) | 2.31      | 1.39  | 0.58         |

| Std MPTA         | \(\text{CH}_4/\text{N}_2\) | \(z_0^*\) (cm\(^3\)/g) | 0.386    | 1.25  | 0.26          |
|                  |         | \(\epsilon_0^*(\text{J/mol})\) | 8085     | 3580  | 8238         |
|                  |         | \(\beta^*\) | 1.88      | 1.45  | 2.06         |

\[a\] 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 \(z_i^*, \epsilon_0^*, \) and \(\beta^*\) 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 $\beta$ (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.

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