New insights into the ideal adsorbed solution theory†

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The GCMC technique is used for simulation of adsorption of CO₂–CH₄, CO₂–N₂ and CH₄–N₂ mixtures (at 298 K) on six porous carbon models. Next we formulate a new condition of the IAS concept application, showing that our simulated data obey this condition. Calculated deviations between IAS predictions and simulation results increase with the rise in pressure as in the real experiment. For the weakly adsorbed mixture component the deviation from IAS predictions is higher, especially when its content in the gas mixture is low, and this is in agreement with the experimental data. Calculated activity coefficients have similar plots to deviations between IAS and simulations, moreover obtained from simulated data activity coefficients are similar qualitatively as well as quantitatively to experimental data. Since the physical interpretation of activity coefficients is completely lacking we show for the first time that they can be described by the formulas derived from the expression for G° for the ternary mixture. Finally we also for the first time show the linear relationship between the chemical potentials of nonideal and ideal solutions and the reduced temperature of interacting mixture components, and it is proved that the deviation from ideality is larger if adsorption occurs in a more microporous system.

1. Introduction

Developed in 1965 by Myers and Prausnitz the Ideal Adsorbed Solution (IAS) approach is still used for prediction of mixture gas adsorption from single component adsorption isotherms, as well as for description of mixture adsorption from the gaseous phase and even from solutions. Moreover the IAS is also capable of predicting adsorption from ternary gas mixtures. The most practical application of this concept is probably the calculation of selectivity, however, it should be remembered that the extensive computational study of Monsalvo and Shapiro proved that the selectivity coefficients calculated from the IAS can deviate from experimental (deviations in the range of 35–45%) thus the IAS estimations should be treated with care.

It was widely proved that in many cases agreement exists between experimentally measured and theoretically calculated (using IAS concept) adsorption isotherms. Thus for example for the mixture of ethane and ethylene adsorbed on 13X molecular sieves, mixture isotherms were measured and the results were compared with the IAS predictions showing excellent agreement. A similar situation occurs, for example, for methane–ethane mixtures adsorbed on the BPL carbon. There is also agreement between simulated and calculated IAS isotherms. Thus, for example, good agreement was observed for GCMC and IAS calculated selectivity coefficients of the Xe–Kr mixture in zeolite NaA. IAS theory also predicts well the GCMC data of binary mixtures of hydrocarbons adsorption (methylene, ethane and propane) in the zeolite silicalite, propane/propylene isotherms on CuBTC MOF, methane, nitrogen and propane mixtures adsorbed on MCM-41 and nanotubes, methane–ethylene mixtures on a porous carbon model (with exception of high pressures), methane, ethane, propane, n- and isobutane adsorbed in silicalite-1, CO₂–N₂, CO₂–CH₄ and CH₄–N₂ adsorbed in ZIFs, CH₄–H₂ on different IRMOFs, O₂–N₂ mixture in C₁₆₈ Schwarzite, methane–ethylene mixtures on MCM-41, CO₂–N₂ and CH₄–N₂ in MOFs and zeolites, CO₂–CH₄ mixtures in pores of activated carbon etc.

Considering the basic assumptions of the IAS it is obvious that this theory predicts good selectivity at low loadings, for the gases having similar molecular volumes, and if the molecules adsorbed do not interact strongly, and the adsorbate–adsorbent system is not too heterogeneous. For this reason, for example, the deviations between the IAS predictions and GCMC results were smaller for the system Xe–Kr (similar dimensions of molecules)
than for Xe–Ar (for adsorption on zeolite NaA). 16 Also since the adsorption capacities of p-xylene (8 molecules per unit cell) and toluene (also 8 molecules per unit cell) are different in PARA silicalite than the capacity for m-xylene (6 molecules per unit cell) the IAS predictions are in fact not so good (compared to the GCMC results) for p-xylene/m-xylene and m-xylene/toluene mixtures. In contrast to the p-xylene/toluene mixture on PARA silicalite, IAS works very well due to the similar adsorption capacities of components. 30

On the subject of selectivity predicted by the IAS model a very interesting paper has been published recently by de Oliveira et al. 31 The authors pointed out the importance of the fact that the pore size distribution (PSD) of components in a mixture can be different from the PSD of individual components, and they proposed a simple mixing rule, assuming that the “contribution” of individual PSD curves to the global adsorption is proportional to the molar fraction of components in the gas phase. The calculated, taking this into account, selectivity can be remarkably different from that obtained from the IAS concept.

It was also proved that the IAS model applied for calculation of the composite binary mixture isotherm from the singe component isotherms does not predict the data adequately if the so called “segregation effect” occurs. 32 It was also shown that for adsorption of the mixtures of CO2, N2, and H2 in zeolite Na-4A IAS predicts that the adsorption selectivity is essentially independent of the gas phase composition. 33 However, the GCMC results show that the selectivity decreases markedly as the gas phase mole fraction of CO2 in the gas mixture increases (note that at 1.0 atm the overprediction of IAS selectivity estimation is 70%). Thus in this case IAS results are accurate only at low CO2 pressures. 33

The IAS predictions strongly depend on the choice of the isotherm model applied for the description of single component adsorption isotherms. 7,12,33–38 To avoid this Chen and Sholl 39 developed the transition matrix Monte Carlo (TMMC) approach but it can be applied only for simulated and not for experimental adsorption data.

As it can be concluded from the short introduction presented above, there is a lack of systematic and complex studies on the IAS concept. Certainly this concept is valid since it has a strong thermodynamic basis, however during calculation of binary isotherms and selectivity coefficients the fundamental assumption of the IAS approach, i.e. that the solution should be “ideal”, is often forgotten. Since the IAS assumes ideality it works well only up to the particular pressure limit. There are attempts in the literature to take nonideality of solution into account. Thus for example, Li et al. 40 used Real Adsorption Solution Theory (RAST) introducing activity coefficients from the Wilson’s theory using the method proposed earlier by van der Vaart et al. 41 However, as it was pointed out by van der Vaart et al. 41 themselves, the Wilson interaction parameters are not only completely different from those found for bulk solutions, but also the physical interpretation of these parameter values is completely lacking. Thus some new solutions in this field should be found. And this is the next purpose of our study.

Therefore, we check the applicability of IAS for description of binary mixture isotherms calculated for adsorption on realistic, so called “Virtual Porous Carbon” (VPC) models proposed recently. 42 Since in real systems it is not simple to achieve systematic and controlled changes in the porosity and/or in the chemical composition of the surface layer, we use molecular simulations. The application of VPC also offers complete knowledge about the pore size distributions (PSD) of applied VPC. This is very important information since the chemical composition of the carbon surface layer and porosity determine the adsorption properties of activated carbons. Summing up, using the VPC and GCMC simulations we are able to generate a series of single and multicomponent adsorption isotherms and next, to use the IAS concept for the description of simulation results. In this way we are able to relate the characteristics of carbons with the range of IAS applicability, we can calculate errors and activity coefficients and finally we can try to relate the values of activity coefficients with some physicochemical characteristics of carbon models. Since based on VPC our studies are limited to activated carbons they are not necessarily valid for other adsorbents.

2. Calculation details

2.1 Simulation boxes

In this work, we use three virtual porous carbon (VPCs) models denoted as d0.5, d0.9 and d1.3 which were described in detail previously. 42 They were generated following the simple Metropolis Monte Carlo method employing one of the most sophisticated carbon force fields, i.e. the environment-dependent interaction potential for carbon (EDIP) proposed by Marks. 43,44 Additionally, based on the d0.9 carbon the series of three gradually oxidized structures was generated using the previously proposed virtual oxidation procedure. 45 For simplicity, only carbonyl groups are investigated (as it was shown by Jorge et al., 46 who considered water adsorption, the type of oxygen-containing groups is not of critical importance, since more complex groups can effectively be represented by simpler sites; a similar conclusion was also provided by Di Biase and Sarkisov 47 who studied the adsorption of CO2 and CH4). The following numbers of carbonyl oxygen atoms were introduced: 52, 104 and 156. These oxidised VPCs were denoted as d0.9_052, d0.9_104 and d0.9_156. All the model carbons (presented schematically in Fig. 1) were placed in a cubicoid simulation box having dimensions $4.5 \times 4.5 \times 4.5$ nm with periodic boundary conditions in all three directions. The porosity of the studied carbonaceous adsorbents was characterised by a geometrical method proposed by Bhattacharya and Gubbins (BG) 48 The implementation of the method was described in detail elsewhere. 42

2.2 Monte Carlo simulations

Due to practical importance 50–53 we consider three binary gas mixtures: CO2–CH4, CO2–N2, and CH4–N2. Their adsorption at 298 K on the above-described model carbons was simulated using the grand canonical Monte Carlo method (GCMC). 54,55
The simulations were performed for the following values of total pressure ($p_{\text{tot}}$): 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9, and 1.0 MPa and for each pressure value different mole fractions of components in the gaseous phase ($y$) were assumed, i.e. 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, and 0.9. The methodology of calculations was analogous to that described previously. Each GCMC simulation run consists of $2.5 \times 10^8$ iterations. The first $1.0 \times 10^8$ iterations are discarded to guarantee equilibration. One iteration is an attempt of the system state change by the randomly selected perturbation: (i) displacement and/or rotation of randomly chosen molecules, (ii) creation of new molecules, (iii) annihilation of randomly chosen existing molecules or (iv) swap move with equal probabilities. We use equal probability for each perturbation to guarantee the condition of microscopic reversibility. Both the adsorbent structure and the molecules of adsorbate are modelled as rigid ones. Table 1 shows all the applied values of the interaction parameters. The Lorentz–Berthelot mixing rules are used for calculation of cross-term energy parameters (with the exception of the C–H interaction between different CH$_4$ molecules – see Table 1 and ref. 58).

From the GCMC simulation results, we determine the average numbers of each kind of adsorbate molecules in the simulation box ($h_i$). These values are used for calculating the absolute adsorption amounts of each component per unit of adsorbent mass ($a_i$) and their mole fractions in the adsorbed phase ($x_i$). Finally, in order to illustrate the efficiency of mixture

Table 1  The values of LJ potential parameters and point charges applied in simulations

<table>
<thead>
<tr>
<th>Geometric parameters</th>
<th>Centre</th>
<th>$\sigma$ [nm]</th>
<th>$\varepsilon/k_B$ [K]</th>
<th>$q/e$</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO$_2$</td>
<td>C</td>
<td>0.2824</td>
<td>28.680</td>
<td>+0.664</td>
<td>57</td>
</tr>
<tr>
<td></td>
<td>O</td>
<td>0.3026</td>
<td>82.000</td>
<td>—</td>
<td></td>
</tr>
<tr>
<td>CH$_4$</td>
<td>C</td>
<td>0.3400</td>
<td>55.055</td>
<td>−0.660</td>
<td>58</td>
</tr>
<tr>
<td></td>
<td>H</td>
<td>0.2650</td>
<td>7.901</td>
<td>+ 0.165</td>
<td></td>
</tr>
<tr>
<td></td>
<td>C–H$^a$</td>
<td>0.3025</td>
<td>30.600</td>
<td>—</td>
<td></td>
</tr>
<tr>
<td>N$_2$</td>
<td>N</td>
<td>0.3310</td>
<td>36.000</td>
<td>−0.482</td>
<td>59</td>
</tr>
<tr>
<td></td>
<td>COM$^b$</td>
<td>—</td>
<td>—</td>
<td>+0.964</td>
<td></td>
</tr>
<tr>
<td>VPC</td>
<td>C$^c$</td>
<td>0.3400</td>
<td>28.000</td>
<td>—</td>
<td>46</td>
</tr>
<tr>
<td></td>
<td>C$^{cd}$</td>
<td>0.3400</td>
<td>28.000</td>
<td>+0.500</td>
<td></td>
</tr>
<tr>
<td></td>
<td>O</td>
<td>0.2960</td>
<td>105.800</td>
<td>−0.500</td>
<td></td>
</tr>
</tbody>
</table>

$^a$ Cross-interaction parameters. $^b$ Centre of mass. $^c$ Non-carbonyl group atom of C. $^d$ Carbonyl group C atom.
separation we also compute the values of equilibrium separation factors:

\[ S_{1/2} = \frac{x_1}{x_2} \frac{y_1}{y_2} \]  

(1)

The adsorbed phase is enriched in the 1st component if \( S_{1/2} > 1 \).

Similarly (i.e. using the analogical Monte Carlo simulation scheme), adsorption isotherms of pure gases (i.e. CO\(_2\), CH\(_4\) and N\(_2\)) are also obtained. We consider the following pressure ranges: \( 1.0 \times 10^{-6} - 1.0 \) MPa for CO\(_2\), \( 1.0 \times 10^{-6} - 25.0 \) MPa for CH\(_4\) and \( 1.0 \times 10^{-6} - 60.0 \) MPa for N\(_2\).

2.3 Thermodynamic background

The thermodynamic background of mixed-gas adsorption and theory of ideal adsorbed solution (IAS) was developed by Myers and Prausnitz\(^1\) in 1965. It is based on the spreading pressure concept associated with adsorption at planar solid–fluid interfaces. For porous adsorbents, as in our case, the thermodynamic formalism was worked out by Myers and Monson.\(^{60}\) According to both approaches the Gibbs adsorption isotherm for a binary mixture can be expressed as (eqn (20) in ref. 1 and eqn (3.16) in ref. 60):

\[ \psi = a_1 \ln f_1 + a_2 \ln f_2 \]  

(2)

where \( a_i, f_i \) are the specific absolute adsorption, the fugacity of \( i \)-th component, respectively, \( \psi \) is the reduced grand potential. In the case of flat adsorbent surfaces\(^3\) it is defined as:

\[ \psi = \frac{A \pi}{RT} \]  

(3)

where \( \pi \) is the spreading pressure, \( A \) is the specific surface area of adsorbent, \( T \) is absolute temperature and \( R \) is the universal gas constant. For porous adsorbents the definition of \( \psi \) is:\(^{60}\)

\[ \psi = \frac{-\Omega}{RT} \]  

(4)

where \( \Omega \) is the grand potential (here it is divided by the mass of adsorbent):

\[ \Omega = F - \sum_i a_i \mu_i = \mu_s - P_{\text{tot}} v_s \]  

(5)

In eqn (5) \( F \) is the specific Helmholtz free energy of the solid phase, \( \mu_i \) is the chemical potential of \( i \)-th adsorbate in the solid phase equal in equilibrium to its chemical potential in the gas phase, \( \mu_s \) is the chemical potential of the solid adsorbent; \( P_{\text{tot}} \) is the pressure in the gas phase and \( v_s \) is the specific volume of the solid phase.

We can also obtain eqn (2) from the Gibbs–Duhem equation written for the pore volume of our adsorbent (the difference between the volume of simulation box and the volume of adsorbent) as \( (T = \text{const.}) \):

\[ \sum_i a_i d\mu_{i,p} - v_p dp_p = 0 \]  

(6)

Here \( v_p \) is the pore volume divided by the adsorbent mass, \( \mu_{i,p} \) is the chemical potential of \( i \)-th adsorbate in the pore volume equal in equilibrium to its chemical potential in the gas phase and \( p_p \) is the pressure inside the pores. From eqn (6) and (2) results where now \( \psi \) is defined as:

\[ \psi = \frac{v_p p_p}{RT} \]  

(7)

Compared to eqn (3) it is seen that \( A \) and \( \pi \) are replaced by \( v_p \) and \( p_p \), respectively. \( p_p \) is a resultant of \( p_{\text{tot}} \) and the interactions of adsorbates and adsorbent.

One should also mention about another thermodynamic approach for the gas adsorption in a porous solid developed by Talu.\(^{61}\) According to this approach the grand potential \( (\varphi) \) is defined as (eqn (16) in ref. 61):

\[ \varphi = \mu_s - \mu^*_s = -RT \int_0^{p_0} \left( \frac{a_i}{p_i} - \frac{v_s}{RT} \right) dp_i \]  

(8)

where \( \mu^*_s \) is the chemical potential of the pure adsorbent at \( p = 0 \). For the absolute adsorption \( v_s \) in the above equations is equal to the sum of the inaccessible solid volume and the pore volume (eqn (36) in ref. 61). In our case \( v_s \) is the volume of the simulation box for which the average numbers of adsorbate molecules were determined (see Section 2.1). Analysing eqn (8) it should be noted that as \( v_s \) does not depend on \( p \), with the increase of \( p \) the value of \( \varphi \) at first will go towards more negative values and then its absolute value will start to decrease, as illustrated in Fig. 2 for a pure gas. As \( \varphi \) has the same value for two different pressures it cannot be regarded as the appropriate definition of the grand potential.

The basic point in the adsorption solution theory is to determine the grand potential. For our case the total pressure \( (P_{\text{tot}}) \) does not exceed 1 MPa. Therefore, we assume that \( f_i \) can
be replaced by the partial pressure \( p_i \). Thus eqn (2) can be written as:

\[
d\psi = \frac{a_1}{p_1} dp_1 + \frac{a_2}{p_2} dp_2 = \left( \frac{a_1 + a_2}{p_{tot}} \right) dp_{tot} + \left( \frac{a_1}{y_1} - \frac{a_2}{y_2} \right) dy_1 \tag{9}
\]

where \( p_i \) is related to \( p_{tot} \) by:

\[
p_i = y_ip_{tot} \tag{10}
\]

\( y_i \) is the mole fraction of the \( i \)-th adsorbate in the gas phase. Having experimentally (or by simulation) determined \( a_1 \) and \( a_2 \) for the mixture as a function of \( p_1 \) and \( p_2 \) (or \( p_{tot} \) and \( y_1 \) ), \( \psi \) can be determined from eqn (9) in different ways and each way should give the same value of \( \psi \), because \( \psi \) is the state function/variable. E.g. choosing \( p_1 \) and \( p_2 \) as independent variables, \( \psi \) is calculated as:

\[
\psi(I) = \int_0^{p_1} \frac{a_1(p_1, p_2 = 0)}{p_1} dp_1 + \int_0^{p_2} \frac{a_2(p_1, p_2)}{p_2} dp_2 \tag{11}
\]

should be equal to that obtained from:

\[
\psi(II) = \int_0^{p_2} \frac{a_2(p_1 = 0, p_2)}{p_2} dp_2 + \int_0^{p_1} \frac{a_1(p_1, p_2)}{p_1} dp_1 \tag{12}
\]

To fulfill this condition, the equality of mixed partials \((\partial(\partial(p_1)/\partial(p_2))_p)/\partial(p_1) = (\partial(\partial(p_2)/\partial(p_1))_p)/\partial(p_2)\) should be satisfied, i.e.:

\[
\frac{\partial (a_1/p_1)}{\partial y_1} = \frac{\partial (a_2/p_2)}{\partial y_1} \tag{13}
\]

or

\[
\frac{\partial (a_1 + a_2)/p_{tot}}{\partial y_1} = \frac{\partial (a_1/y_1 - a_2/y_2)}{\partial y_1} \tag{14}
\]

Eqn (13) and (14) result from the fact that according to eqn (9) \((\partial^2(p_1)/\partial p_2) = a_1/p_1 \) and \((\partial^2(p_2)/\partial p_1) = a_2/p_2 \). Checking of these equalities is very important – if they are not fulfilled it means that the results are not accurate or the theory expressed by eqn (9) does not hold for a given system. It should be stated that up to our knowledge no such tests have been published to date in the papers reporting the results of the IAS concept.

For the mixing process carried out at constant grand potential \( \psi \) and \( T \) the two equalities hold:

\[
\psi = \psi_1^0 = \psi_2^0 \tag{15}
\]

where \( \psi_i^0 \) refers to \( \psi \) in the single gas adsorption and is given by eqn (9) written for that case as:

\[
\psi_i^0 = \int_0^{p_i^0} \frac{a_i}{p} dp \tag{16}
\]

From the equality of chemical potentials of the adsorbate in the gas phase and in the adsorbate solution it results that the pressure of a pure \( i \)-th component corresponding to \( \psi \) and \( p_i^0 \) is given by eqn (5.4) in ref. 60 and (25) in ref. 61 for the ideal gas phase:

\[
p_i^0 = \frac{p_i}{y_i x_i} = \frac{y_ip_{tot}}{y_i x_i} \tag{17}
\]

where \( p_i \) is the partial pressure of \( i \) in the gas mixture, \( x_i \) and \( y_i \) are the mole fraction and the activity coefficient of the \( i \)-th component in the adsorbed solution, respectively.

In the case of IAS it is assumed that \( \gamma_1 = 1 \) and only the second equality of eqn (15) (i.e. \( \psi_1^0 = \psi_2^0 \)) is taken into account. Thus, from eqn (15)–(17) \( x_i \) as a function of \( y_i \) and \( p_i \) is obtained. For \( \psi \) the total amount of adsorbed gases \( (a) \) is given by eqn (4.14) in ref. 60:

\[
a = \frac{1}{x_1/a_1^0 + x_2/a_2^0} \tag{18}
\]

where \( a_i^0 \) is the amount of the adsorbed \( i \)-th component in the absence of another component calculated for the same \( \psi \). The amount of the \( i \)-th component adsorbed from the mixture \( (a_i) \) is calculated as:

\[
a_i = x_i a \tag{19}
\]

In the case of nonideal adsorption solutions the activity coefficients \( \gamma_1 \) and \( \gamma_2 \) are calculated from the equalities (15) taking the experimental (in our case determined from the GCMC simulation) values of \( x_i \).

2.4 Checking of equality of \( \psi(1) \) and \( \psi(II) \)

We tested the consistency of our data by comparing \( \psi(I) \) with \( \psi(II) \) calculated using eqn (11) and (12). In those calculations \( a_1/p_1 \) and \( a_2/p_2 \), obtained from the direct simulation of binary mixtures adsorption, were approximated independently as a function of \( p_1 \) and \( p_2 \) using the empirical function:

\[
g_i(p_1,p_2) = \sum_{k=1}^{N} \frac{a_{m,k}K_{a,k}}{1 + (K_{a,k}p_1)^{n_{a,j,k}} + (K_{a,k}p_2)^{n_{a,j,k}}} \tag{20}
\]

where \( g_i = a_i/p_i \) \( K_{a,k} \) and \( n_{a,j,k} \) are the best-fit parameters (not negative), \( N \) usually 2 or 3 was chosen to obtain a good fit \( (R^2 > 0.9999) \). Among other tested functions eqn (20) gave the best fit. It should be noted that eqn (20) is not symmetric, i.e. \( \partial g_i/p_1 \neq \partial g_i/p_2 \) (see eqn (13)) even in the case of a very good fit. Therefore, when this function is used one should expect smaller or higher differences between \( \psi(I) \) and \( \psi(II) \). On the other hand, the use of a function with a symmetry property would have no sense.

The smallest deviation of \( \psi(I) \) (eqn (11)) from \( \psi(II) \) (eqn (12)) was observed for the carbon d0.5 (0.13–1.2%), the highest deviation for the systems: d0.9_104 and adsorption of CO2-N2 mixture (11%) and d0.9 and CH4-N2 mixture (10%), although the fit quality for those systems was very high \( (R^2 > 0.9996) \). No regularity was observed, e.g. for the system d0.9_156 and CH4-N2 mixture only 0.16% deviation was observed. Thus generally we can conclude that the simulation adsorption results can be described by eqn (9).

2.5 IAS calculations

To find \( x_i \) from the second part of equalities (15) and eqn (16) and (17) the single-component isotherms should be approximated by some mathematical equation. In this work, we used
where $a_{m,k}$, $K_i$ and $n_i$ are the best-fit parameters. During the fitting isotherms by eqn (21), we minimised the mean relative error (MRE):

$$MRE = \frac{1}{NP} \sum_{i=1}^{NP} \left( \frac{a_{i,app} - a_{i,sim}}{a_{i,sim}} \right) \times 100\%$$

where NP is the number of points of a simulated isotherm, $a_{i,app}$ and $a_{i,sim}$ are the approximated by eqn (21) and simulated adsorption amount for the $i$-th point, respectively. The obtained values of the best-fit parameters are collected in Table S1 in the ESL. As one can see, in the case of the considered simulated adsorption isotherms of pure CO$_2$, CH$_4$ and N$_2$, MRE does not exceed 0.5%.

It should be noted that for the gas which is less adsorbed $p_i^0$ ($\psi$) is always higher than that for the more adsorbed gas, as resulted from eqn (16). The gas mixture pressure corresponding to the same $\psi$ is between these two pressures. In our case we have found that the pressure of the less adsorbed gas can be much higher (even 30 times) than that of the mixture pressure. Therefore the adsorption of CH$_4$ and N$_2$ were simulated also for high pressure values. Substituting eqn (21) into (16) we get:

$$\psi_i^0 = \sum_{k=1}^{3} \frac{a_{m,k} \ln\left(1 + \left(Kkip_i^0\right)^{n_k}\right)}{\mu_k}$$

Taking into account eqn (17) with $\gamma_i = 1$, $x_1$ was found by solving the second part of equalities (15). Having $x_1$ at the equilibrium, we calculated the equilibrium separation factor $(S_{ij})$ from eqn (1) and the adsorption amounts of components ($a_i$) from eqn (19).

In order to illustrate the differences between the predictions of IAS theory and the results of direct simulation of mixtures adsorption for each considered point (defined by the combination of $p_{tot}$ and $y_i$ values) we calculated the relative “errors” of the components adsorption amounts and equilibrium separation factors:

$$\Delta(q(p_{tot},y_i)) = \frac{|q_{IAS}(p_{tot},y_i) - q_{sim}(p_{tot},y_i)|}{q_{sim}(p_{tot},y_i)} \times 100\%$$

where $q$ denotes the considered quantity ($a_i$ or $S_{ij}$) and subscripts “IAS” and “sim” relate to the values obtained from IAS theory and from the simulations, respectively.

### 2.6 The activity coefficients of components in the adsorbate solution

The observed deviations between the IAS prediction and the “experimental” (simulated) adsorption from the gas mixture can be attributed to the nonideal behaviour of adsorbates in the “adsorbate solution”. The nonideal behaviour of the gas mixture is of minor importance because the pressure was not high ($\leq 1$ MPa).

The activity coefficients $\gamma_1$ and $\gamma_2$ of the components of the adsorbate solution were calculated by solving the equalities (15) with the substituted eqn (16) and (17) ($x_1$ was taken from the simulation experiment). To reduce the approximation errors, we calculated $\psi$ for the mixture not from eqn (11) or (12) but using the equation:

$$\psi = \int_{0}^{p_{tot}} \frac{a_1 + a_2}{p} dp \quad y_1 = \text{const.}$$

Thus, two approximations ($b_1-b_2$ are the best-fit parameters).

To analyze the dependencies $\gamma_i(x_1)$ and $\gamma_i(x_2)$ at constant $\psi$ they were calculated as follows. For a given value of $y_1$ ($p_{tot}$ is a variable) we approximated $x_1$, $\gamma_1$ and $\gamma_2$ as a function of $\psi$ using the function:

$$z = \left(\frac{\psi}{\psi_1}\right)^{c_1} \exp(c_2\psi)$$

where $z = x_1$, $\gamma_1$ or $\gamma_2$ and $c_1$-$c_2$ are the best-fit parameters. In most cases, eqn (28) worked satisfactorily. Next $x_1$, $\gamma_1$, $\gamma_2$ were calculated from eqn (28) for a given $\psi$ chosen from the range common for all $y_1$ values: $\psi_{min} (y_1 = 0.9)$, $\psi_{max} (y_1 = 0.1)$. The obtained set of 9 points was finally approximated by the existing formulas relating $\gamma_i$ with $x_i$.

### 3. Results and discussion

Fig. 3 shows the BG pore size distribution curves of studied VPC samples. One can observe that all the studied samples are strictly microporous (pores with $d_{eff}$ below 2 nm). The distribution of microporosity is the widest for the sample d0.5, and the narrowest for d1.3. It is also important that the virtual oxidation procedure does not change the geometric PSD curve remarkably, and for the samples d0.9, d0.9_052, d0.9_104 and d0.9_156 we observe practically the same PSD.

In Fig. 4 a comparison of the simulated single component adsorption isotherms ($T = 298$ K) of the studied gases on all the VPC models is shown. As one can see, for all the studied carbons adsorption decreases in the following order: CO$_2$ < CH$_4$ < N$_2$. The narrowing of pores and shifting of the PSD toward smaller pore diameters (see Fig. 3) leads to progressive changes in the shapes of simulated adsorption isotherms, i.e. isotherms from linear (i.e. Henry’s type) become more characteristic to the Type I.

The IAS predictions were based only on the grand potential $\psi^0$ for pure gases calculated from eqn (23). As mentioned above...
Fig. 2) the Talu’s grand potential $j^0$ can show an extremum. Fig. S1 in the ESI† presents the comparison of $j^0$ for all the simulated single gas adsorption isotherms. Here $j^0$ is plotted in the pressure range which results from the condition $j^0$(gas 1) = $j^0$(gas 2). The minima of $j^0 = f(p)$ are clearly seen in the case of N$_2$ adsorption on all the considered carbons and also of CH$_4$ adsorption on the d1.3 structure. In Fig. 5 $\psi^0$ and $\phi^0$ for CO$_2$ and N$_2$ versus $x_{CO_2}$ are shown in the range close to the simulated value of $x_{CO_2}$. The intersection point determines $x_{CO_2}$ according to the IAS theory. It is seen that $\phi^0$ used as the grand potential yields in some cases two or no solution depending on the gas mixture composition (p$_{CO_2}$). This is the reason why further in the text we discuss only the results based on $\psi$ defined according to the Myers and Monson formalism.

The results comparing IAS predictions and simulations are collected in Fig. 6 (for d0.9 carbon) and Fig. S2–S6 in ESI† (for other carbons). One can see that for all the systems the adsorption values of the better adsorbed compound are predicted by the IAS concept very well (we call the better adsorbed compound i.e. CO$_2$ for CO$_2$–CH$_4$ and CO$_2$–N$_2$ and CH$_4$ for CH$_4$–N$_2$ mixtures as the 1st one). In contrast, the reverse situation is observed for the weakly adsorbed compound (called as the 2nd one). The differences between the results of simulation and the IAS predictions increase with the rise in total pressure and the mole fraction of the first component in the gas phase. Similar behaviour (increasing differences between simulation results and the IAS predictions with the rise in p$_{tot}$ and y$_1$) is observed in the case of equilibrium separation factors.

To compare the differences between the IAS and simulations we calculate the average errors (collected in Fig. 7) of $a_1$, $a_2$ and $S_{1/2}$. The errors were averaged for each total pressure value in two groups; for the low mole fraction of the 1st component

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{fig3.png}
\caption{Comparison of the pore size histograms for all the considered VPCs (subsequent histograms were shifted by 0.15 from the previous ones).}
\end{figure}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{fig4.png}
\caption{Comparison of single component CO$_2$, CH$_4$ or N$_2$ adsorption isotherms on all the considered VPCs (T = 298 K). Only the regions for a pressure of up to 1 MPa are shown.}
\end{figure}
(y_1 < 0.5) and for high y_1 values (y_1 ≥ 0.5). The analysis of the data from Fig. 7 shows that the errors generally increase with the rise in pressure. Moreover, the error of equilibrium separation factors calculated by using the IAS is mainly caused by problems in calculation of the second component adsorption. The errors for those two values are similar and (independently from the total pressure) distinctly higher at larger mole fractions of the first component in the gas phase. Regarding the mixtures the deviations decrease in order: CO_2–CH_4, CO_2–N_2, CH_4–N_2. For the second component the deviation is higher, especially when its content in the gas mixture is low. This observation is in agreement with experimental data published by Harlick and Tezel, who concluded that when one component of a mixture is strongly adsorbed and the other component is weakly adsorbed, theoretical models (among them the IAS) do not predict the adsorption behaviour of the weakly adsorbed component well. One can also see that the highest deviations are observed for d0.9 and its modified forms.

Fig. 5 Visualisation of x_{CO_2} finding according to the IAS theory – searching of equality \( \psi_1^0 = \psi_2^0 \) (Myers and Monson formalism) or \( \varphi_1^0 = \varphi_2^0 \) (Talu formalism) on the example of d0.9 carbon and CO_2–N_2 mixture at \( p_{tot} = 1 \) MPa and for selected \( \chi_{CO_2} \) values. The vertical dashed lines represent \( x_{CO_2} \) value obtained for the simulation mixture adsorption. The grand potentials (eqn (16)) and \( \psi^0 \) (eqn (8)) are calculated for hypothetical values of CO_2 mole fractions in the adsorbed phase \( x_{CO_2} \) – formally \( \psi_{CO_2} = p_{tot} x_{CO_2}/C_1 \) and \( \psi_{N_2} = p_{tot} (1 - x_{CO_2})/(1 - x_{CO_2}) \) (eqn (17) for \( \gamma = 1 \)). The curves plotted for the \( x_{CO_2} \) range correspond to the range of pressure simulated for single components adsorption (i.e. \( \phi_{CO_2} \leq 1 \) MPa and \( \phi_{N_2} \leq 60 \) MPa).
Fig. 6  Comparison of the results simulated directly for all the considered gas mixtures (points) and the predictions of IAS theory (planes) for the d0.9 carbon. The maps of the relative errors ($\Delta$ – eqn (24)) for the values of component adsorption amounts ($\Delta(a_i)$) and equilibrium separation factors ($\Delta(S_{ij})$) obtained from the IAS theory.
Fig. 7 Comparison of the average relative errors (Δav) in the values of: (i) mixture components adsorption amounts (a₁ – blue and a₂ – red) and equilibrium separation factors (S_{1/2} – black) calculated from the IAS theory. The errors were averaged for each total pressure value in two groups: (i) for the mol fraction of the 1st component in gaseous phase (y₁) below 0.5 (open symbols) and (ii) for y₁ ≥ 0.5 (full symbols). The 1st component is CO₂ for CO₂–CH₄ and CO₂–N₂ mixtures and CH₄ for the CH₄–N₂ mixture.
(d0.9.052, d0.9.104, d0.9.156). The modification of d0.9 practically has no effect on the deviation.

It is obvious that the values of errors can correlate with activity coefficients. The plots $\gamma_i = f(p_{\text{tot}}, y_1)$ for all the systems can be found in Fig. 8 (for raw carbons) and in Fig. S7 in ESI† (oxidised carbons). They are similar to the deviations. As an example in Fig. 9 we show the dependence between the average relative errors for adsorption of the weakly adsorbed compound (IAS calculation) and the average values of $RT\ln\gamma_2$.

Before we discuss the activity coefficients calculated from the simulated data we present an example showing that the plots of activity coefficients calculated from GCMC are realistic. In Fig. 10 the comparison of our simulated data for the CO$_2$–CH$_4$ mixture at constant gas mixture pressure ($p_{\text{tot}} = 0.5$ MPa, $T = 298$ K) with those obtained experimentally by Buss$^{44}$ for activated carbon A35/4 at similar pressure ($p_{\text{tot}} = 0.53$ MPa, $T = 293$ and 313 K) is shown. It is seen that the magnitudes of $\gamma_{\text{CO}_2}$ and $\gamma_{\text{CH}_4}$ on $x_{\text{CO}_2}$ are similar. The most

![Fig. 8](image1.png) Comparison of calculated activity coefficients for mixture adsorption on unoxidised carbons. The grey planes represent $\gamma = 1$.

![Fig. 9](image2.png) Dependence between the average relative errors for the values of the 2nd component adsorption amount predicted by IAS theory $- \Delta_{av}(a_2)$ (the data are averaged for all the considered simulation points) and average values of activity coefficients of this component in the mixture (formally $RT\ln\gamma_2$). The dashed line is drawn to guide the eye.
similar to experimental data, quantitative as well as qualitative
dependence of $\gamma_{\text{CO}_2}$ and $\gamma_{\text{CH}_4}$ on $x_{\text{CO}_2}$ is found for d0.9 carbon.
According to Buss data, the temperature effect on $\gamma_{i}$ is insignificant.
It should be noted here that for this case simulation data are very similar to the real ones.
However, not for all the carbons the changes of $\gamma$ with $x$ are the same as shown in Fig. 10.
This is seen while analysing another set of calculated $\gamma_{i}$ for the $\text{CO}_2$–$\text{CH}_4$ adsorption on micro-porous Norit RB1 activated carbon found in ref. 41. The dependence of $\gamma_{\text{CO}_2}$ and $\gamma_{\text{CH}_4}$ on $x_{\text{CO}_2}$ at constant $\psi$ ($\psi = 3,4$ and 5 mmol g$^{-1}$) is shown in Fig. 7 in ref. 41. The nature of dependence is different from ours (Fig. 11 and Fig. S8 and S9 in ESI$^1$). Moreover, in our case the influence of $\psi$ on $\gamma_{i}$ is observed, whereas in the case of ref. 41 there is no such influence (with one exception $\gamma_{\text{CH}_4}$ for $x_{\text{CO}_2} = ca.0.9$).

In both papers cited above the authors additionally applied the Wilson equation for a binary mixture to fit the activity coefficients. However, as pointed out by van der Vaart et al.$^{41}$ the Wilson interaction parameters are not only completely different from those found for bulk solutions, but also the physical interpretation of these parameter values is completely lacking. Thus some new solutions in this field should be found. Surprisingly the fit of activity data at constant $\psi$ failed$^{41}$ whereas those at constant $p$ were fitted satisfactorily$^{64}$ – probably it is a coincidence. However, as Myers pointed out,$^{65}$ the use of Wilson equation is justified only at $\psi =$ const., because only in that case one gets $x_i d \ln \gamma_1 + x_3 d \ln \gamma_2 = 0$ – the basis for Wilson’s equation derivation.

Another dependence of $\gamma_{i}$ on $T$, $\psi$ and $x_3$ was proposed by Siperstein and Myers.$^{66}$ However, at $T$, $\psi =$ const it reduces to the one constant Margules equation ($\ln \gamma_1 \sim x_3^2$). Such equation gives mirror images of $\gamma_1$ and $\gamma_2$ and for the liquid mixtures it is valid only for the similar components.

Thus, for description of our data we have tried the two-constant Margules equations:$^{67}$

$$\ln \gamma_1 = (A - 3B)(1 - x_1)^2 - 4B(1 - x_1)^3$$
$$\ln \gamma_2 = (A - 3B)x_1^2 + 4Bx_1^3$$

where $A$ and $B$ are the parameters of the Redlich–Kister expansion of the molar excess Gibbs free enthalpy of the two component mixture:$^{67}$

$$\frac{G^e}{RT} = x_1 x_2 \left(A + B(x_1 - x_2) + C(x_1 - x_2)^2 + \ldots\right)$$

Here $A$ and $B$ are the expansion parameters. Unfortunately, it is not possible to fit our data with eqn (29) and (30). However, it is not surprising that the equations elaborated for the binary liquid mixtures do not work – in such mixtures interactions between components 1 and 2 of the type: 1-1, 1-2 and 2-2 occur. In the adsorbate solutions also the interactions with the adsorbents i.e.: 1-adsorbent and 2-adsorbent are present. Thus, we postulate that the equations developed for the ternary liquid mixtures are more suitable. For the adsorbate solution the third constituent would be the vacancies on the surface. However, they cannot be treated as a full constituent. For example, taking into account eqn (26) from ref. 1 the term $x_i d \gamma_i$ would have to appear. For vacancies the quantity $a_3^q$ does not exist. Therefore we still treat the adsorbate solution as the binary mixture but somehow we have to introduce the interactions of gases with the adsorbent. The simplest way it seems to take just the expression for $G^e$ for the ternary system. Following this, two expansions of $G^e$ for the ternary system were tested.

The first one is the extension of eqn (31) in the following way:

$$\frac{G^e}{RT} = x_1 x_2(x_1 A_{12} + B_{12}(x_1 - x_2)) + x_1 x_3(x_1 A_{13} + B_{13}(x_1 - x_3)) + x_2 x_3(A_{23} + B_{23}(x_2 - x_3))$$

The second one is the truncated formula:$^{58}$

$$\frac{G^e}{RT} = x_1 x_2(x_1 A_{21} + A_{12}) + x_1 x_3(x_1 A_{31} + A_{13}) + x_2 x_3(A_{23} + A_{32} + A_{31})$$

In eqn (32) and (33) the parameters $A_{ij}$ are not the same. The $\ln \gamma_{i}$ is given by the partial derivative of $G^e$: $\ln \gamma_{i} = (\partial (nG^e/RT)) / (\partial n_i)_{T,\psi,y_{j\neq i}}$, where $n = n_1 + n_2 + n_3$. Thus we get:
(a) from eqn (32):
\[
\ln g_1 = -x_1x_2(A_{12} - 2B_{12}(1 + x_2 - x_1)) \\
- x_1x_3(A_{13} - 2B_{13}(1 + x_3 - x_1)) + x_3(A_{12} - x_2B_{12}) \quad (34) \\
+ x_3(A_{13} - x_3B_{13}) - x_2x_3(A_{23} + 2B_{23}(x_2 - x_3)) 
\]

\[
\ln g_2 = -x_1x_2(A_{12} + 2B_{12}(1 + x_2 - x_1)) \\
- x_2x_3(A_{23} - 2B_{23}(1 + x_3 - x_2)) + x_1(A_{12} + x_1B_{12}) \quad (35) \\
+ x_3(A_{23} - x_3B_{23}) - x_1x_3(A_{13} + 2B_{13}(x_1 - x_3)) 
\]

(b) from eqn (33):
\[
\ln g_1 = x_1^2(A_{12}(1 - 2x_1) - 2A_{32}x_3) + x_3^2(A_{13}(1 - 2x_3) - 2A_{23}x_2) \\
+ 2(1 - x_1)x_3(A_{21}x_2 + A_{31}x_3) \quad (36) 
\]

Here \( \gamma_2 \) is obtained from eqn (36) by exchanging subscripts 1 with 2.

It can be noticed that the above activity coefficients satisfy the condition \( \lim_{\psi \to 0} \gamma_i = 1 \), whereas we should not expect that the limit of \( \gamma_i \) at \( \psi \to 0 \) is 1 because of the presence of the 3rd component (adsorbent). The condition \( \sum \gamma_i d \ln \gamma_i = 0 \) is satisfied if we take into account the 3rd component.
To avoid some ambiguities in determining the maximum concentration of vacancies, \( a_{\text{max}} \), needed for the calculation of molar ratios in the ternary system, we decided to treat \( a_{\text{max}} \) as a fitting parameter. Thus, \( x_3 \) was expressed as \( x_3 = \frac{1}{C_0} \left( \frac{a_1 + a_2}{a_{\text{max}}} \right) \), whereas \( x_i \) and \( x_2 \) were replaced by \( x_i \) for the binary mixture, \( x_i(\text{bin}) = \frac{a_i}{(a_1 + a_2)} \), using the relation: \( x_i = x_i(\text{bin}) (1 - x_3), \ i = 1, 2 \); \( x_i(2) \) was calculated as \( x_i = \frac{a_i}{(a_1 + a_2)} \).

For both assumed \( G^\text{ex} \) expansions the fit is sufficiently good. In the case of \( G^\text{ex} \) given by eqn (32) the changes of \( a_{\text{max}} \) are smaller than in the case of eqn (33) (Table S2 in ESI†) probably because we have excluded the parameter \( B_{12} (B_{12} = 0) \), which had no influence on the quality of the fit. However, it was also found that \( a_{\text{max}} \) can be changed in a wide range and this change does not influence the quality of the fit. It means that the

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**Fig. 12** Correlations between average values of activity coefficients (formally \( RT \ln g \)) and critical temperatures \( (T_{C1} \times T_{C2})^{1/2} / T \) for mixture components for all the considered carbons. \( T = 298 \) K is the temperature of simulation. 1st component is CO\(_2\) for CO\(_2\)--CH\(_4\) and CO\(_2\)--N\(_2\) mixtures and CH\(_4\) for the CH\(_4\)--N\(_2\) mixture. The dashed lines are drawn to guide the eye.
parameters of the model are strongly correlated. The optimal values of $a_{\text{max}}$ seem to be reasonable, because they are higher than the maximum of $(a_1 + a_2)$ obtained for the gas mixtures or $a_i$ obtained for pure gases at the highest investigated pressure. Finally, since as it was mentioned by different authors, the physical interpretation of activity coefficients is not simple and sometimes even completely lacking, we try to relate activity coefficients with the physicochemical properties of interacting molecules. The correlation between average In $\gamma_1$ or In $\gamma_2$ and the function of critical temperatures ($T_{C1} \times T_{C2})^{1/2}/T$ (where $T$ is the temperature of adsorption) is shown in Fig. 12.

The explanation of the origin of this correlation can be as follows. Empirical combining laws relating the force constants (collision diameters $\sigma$ and energy of interaction $\epsilon$) between molecules 1 and 2 can be given as follows:

$$\sigma_{12} = \frac{1}{2}(\sigma_{11} + \sigma_{22})$$

$$\epsilon_{12} = (\epsilon_{11} \times \epsilon_{22})^{1/2}$$

On the other hand, application of the principle of corresponding states leads to the relation of the type:

$$\epsilon_i \sim TC_i$$

To take into account that the states of both interacting gases are different we must apply the reduced temperature and finally we can write eqn (38) in the form:

$$\epsilon_{12} \sim \left(\frac{T_{C1}T_{C2}}{T}\right)^{1/2}$$

On the ordinate in Fig. 12 the difference between the chemical potentials of ideal and real mixture is plotted and the correlation shows that this difference, i.e. the deviation of the system from ideality, depends on the value of the energy of intermolecular interactions between the components of a mixture. It is interesting that for almost all the studied systems (d1.3 is the exception) the strongly adsorbed compound (1st compound in Fig. 12) behaves more ideally than the second mixture component, adsorbed weakly. Thus CH$_4$ in the mixture with N$_2$ and CO$_2$ in both the remaining mixtures are more perfect than N$_2$ and CH$_4$. This is caused by the mechanism of adsorption observed on snapshots (not shown). The 1st component behaves more ideally since in this case interactions 1-1 dominate as observed for a pure compound. In contrast, component 2 is mainly surrounded by the molecules of component 1 thus 1-2 interactions cause imperfection. The rise in reduced temperature has a strong influence on the activity of the weakly adsorbed component, and this component to a larger extent deviates from ideality than the strongly adsorbed one. It can also be seen that with the shift of the PSD plot (Fig. 3) toward smaller micropores [i.e. from d0.5 down to d1.3] we observe larger deviation from ideality for both the components. In the case of d1.3 carbon with the rise in reduced temperature of the interacting mixture components the deviation from ideality is the largest among all the studied systems; moreover, it is also seen for the strongly adsorbed compound. Thus we can conclude that with the rise in microporosity of carbon the nonideality of the adsorbed solution increases.

4. Conclusions

Using GCMC simulations of CO$_2$–CH$_4$, CO$_2$–N$_2$ and CH$_4$–N$_2$ mixtures, adsorption (at 298 K) on six VPC models was studied. The models differ with porosity and with the composition of carbon surface layers (oxygen content). Next, it is shown that the simulated isotherms obey the fundamental condition of IAS application (eqn (5)). The deviations between IAS predictions and simulation results increase with the rise in pressure. It is also shown that for the second component the deviation from IAS predictions is higher, especially when its content in the gas mixture is low, and this is in agreement with the experimental data published by Harlick and Tezel. The calculated activity coefficients have similar plots to deviations between IAS and simulations. The calculated from simulated data activity coefficients are similar qualitatively as well as quantitatively to experimental data published by Buss. Finally we show that the calculated of activity coefficients can be described by the formulas derived from the expression for $G^*$ for the ternary mixture (eqn (32) and (33)). The deviation between chemical potentials of nonideal and ideal solutions increases with the rise in reduced temperature of interacting mixture components, and the deviation from ideality is larger if adsorption occurs in a more microporous system.

Acknowledgements

S.F., A.P.T. and P.A.G. acknowledge the use of the computer cluster at Poznań Supercomputing and Networking Centre (Poznań, Poland) as well as the Information and Communication Technology Centre of the Nicolaus Copernicus University (Toruń, Poland). S.F. gratefully acknowledges financial support from Iuventus Plus Grant No. IP2012 034872 from the Polish Ministry of Science and Higher Education.

References
