

Article Multi-Compound H₂, CH₄, and N₂ Adsorption Analysis

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Abstract: In order to study the purification of hydrogen and its separation from gas mixtures by adsorption, different models describing the adsorption equilibrium of gas mixtures have been tested; seven of them have been compared with experimental multi-component data obtained from the literature. The measurements include three-component mixtures of hydrogen, nitrogen, and methane. All the models used in this study are purely predictive; such models are competitive isotherm models which use only the previously obtained coefficients of the single-component isotherms. A mathematical description of each model is developed and discussed. Based on the results of numerical experiments, an analysis of how best to apply the Sips multi-component approach and the Ideal Adsorbed Solution theory is developed. A discussion on the ability and accuracy of the different models to describe the multi-component adsorption equilibria is developed. Based on this research, the Jovanovic model, which best reproduces the experimental results of the adsorption equilibrium in all cases, can be recommended as the most appropriate to use.

Keywords: adsorption equilibrium; gas mixture; modelling; numerical experiment



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1. Introduction

Hydrogen has recently attracted attention as a future-generation energy carrier for both mobile and stationary power sources [1–3]. A fundamental requirement for the common use of hydrogen is that it must be purified of impurities; this requirement is particularly important for its application in fuel cells. However, in many cases, hydrogen is not absolutely purified from other gases, such as carbon dioxide or methane; when hydrogen production results in gas mixtures, the hydrogen must be separated before use.

Physisorption phenomena of gas mixtures on inert porous solids, such as zeolites and activated carbons, provide the basis for a variety of gas separation processes [4,5]. The separation effect is based on the selective adsorption of one species in the mixture [6–8]. The design and the implementation of separation processes rely on the modelling of multicomponent adsorption equilibria and kinetics. As the prediction of the multi-component adsorption kinetics, any error in the former would lead to a significant error in the latter [9]. Predicting a multi-component equilibrium based on information derived from the analysis of purecomponent adsorption data is therefore a major challenge [10]. Purely predictive models are competitive isotherm models which use only the coefficients of the single-component isotherms; such models allow for the prediction of a competitive isotherm behaviour by knowing only the pure-component adsorption behaviour.

The major objective is to describe any multi-component adsorption equilibrium based on the results of pure-component adsorption isotherms, as obtained in a previous work [11]. Different models have been used to correlate pure/single-component adsorption data and to subsequently predict the multi-component equilibrium; some of them consider an ideal behaviour of the system without taking into account the possible sources of non-ideal behaviour, such as the adsorbate–adsorbate interactions in the adsorbed phase, the heterogeneity of the adsorbent surface, the differences in the molecular size of the adsorbates, or the loss of symmetry [12–15].

In order to achieve the main goal in this study, the features of the application of some of the selected models for gas mixture equilibria have been developed and discussed. In particular, the different types of the extended Sips' equation have been discussed. The possibility of using different single-adsorption models in the Ideal Adsorbed Solution (IAS) and Fast-IAS theories is also developed. A comparison between experimental data (for a ternary mixture containing hydrogen, nitrogen, and methane gases) and the models is performed to check the ability of the different models to predict competitive equilibria using the single-component identified parameters.

2. Modelling

Models and correlations for mixed-gas adsorption should be able to predict the equilibrium amount adsorbed for each component in the mixture from corresponding pure-gas isotherms within a given range of operating temperatures and pressures. As mentioned above, all the models used in this study are purely predictive. A purely predictive model is a competitive isotherm model which uses only the coefficients of the single-component isotherms; such a model allows the prediction of a competitive isotherm behaviour knowing only the single-component adsorption behaviours. Therefore, for gas mixtures described by purely predictive models, the same assumptions as in single-gas adsorption isotherms are considered. Both the description and the discussion on the ability of different models to describe the single-gas adsorption behaviour are given in a previous work [11]. Most of the models used in this study have been developed for the description of single-gas adsorption, and then extended to describe the adsorption equilibrium of gas mixtures.

2.1. Extended Langmuir Equation

The Langmuir isotherm for single gas adsorption can be extended to an *N*-component mixture:

$$Q_{i} = Q_{max,i} \frac{b_{i} f_{i}}{1 + \sum_{j=1}^{N} b_{j} f_{j}}$$
(1)

Markham and Benton [16] first established this correlation for binary mixtures. The assumption of an ideal localized monolayer is made. The system behaviour is defined by the partial fugacity, f_i , of each component. Parameters b_i and $Q_{max,i}$ are the affinity and the saturation capacities of each component, respectively; both are obtained from single-compound isotherms.

The extended Langmuir equation might be the simplest model for multi-component adsorption. However, this model is inadequate for representing a number of real adsorption systems. Sometimes, the Langmuir equation cannot fully describe the adsorption data of single components either. In addition, the thermodynamic consistency requires that the saturation adsorption capacity is the same for all components [17], but such an assumption is unrealistic for molecules of widely different sizes.

2.2. Extended Freundlich Equation

The extended Freundlich model for pure-gas adsorption equilibria [11] has been proposed for multi-component systems [18,19]. The IAS theory is herein used to obtain the isotherm in the case where all the components have the same Freundlich exponent, *n*. For an *N*-component mixture, the result can be written:

$$Q_{i} = \frac{\overline{n} \left(\frac{b_{i}}{n}\right)^{1/\overline{n}} f_{i}}{\left[\sum_{j=1}^{N} \left(\frac{b_{j}}{n}\right)^{1/\overline{n}} f_{j}\right]^{1-\overline{n}}}$$
(2)

In the present case, the *n* parameters in the single-gas Freundlich adsorption isotherm for hydrogen, nitrogen, and methane, achieve values very close to one another [11]. At 298 K, for example, this parameter has a value of 1.002, 1.275, and 1.624 for hydrogen, nitrogen, and methane, respectively. We therefore considered its average value: $\bar{n} = \sum_{j=1}^{N} n_j / N$.

2.3. Extended Sips (Langmuir–Freundlich Equation)

The extended Sips model for an *N*-component system gives:

$$Q = Q_{max,i} \frac{(b_i f_i)^{\frac{1}{n_i}}}{1 + \sum_{j=1}^N (b_j f_j)^{\frac{1}{n_j}}}$$
(3)

The parameter b_i is the average association constant and n_i is the heterogeneity parameter obtained from the single-component Sips equation for each species [20]. The Sips model is generally derived as an empirical model; however, Sips analysed the model using the Stieltjes transform and found that the heterogeneity parameter, n, corresponds to the width of a symmetrical quasi-Gaussian distribution of affinity constants, which means that the Sips model treats the adsorbent surface as an energetically heterogeneous surface. The Jaroniec's extension of the model for gas mixtures gives [21]:

$$Q_{i} = Q_{max,i} \frac{b_{i} f_{i}}{1 + \sum_{j=1}^{N} b_{j} f_{j}} \times \frac{\left(\sum_{j=1}^{N} b_{j} f_{j}\right)^{n}}{\left(1 + \sum_{j=1}^{N} b_{j} f_{j}\right)^{n}}$$
(4)

where $\overline{n} = \sum_{j=1}^{N} n_j / N$.

The extended Sips model is known to be purely predictive, meaning the capacity, heterogeneity, and affinity parameters used are obtained from the single-component behaviour [11].

2.4. Extended Jovanovic–Freundlich Equation

The model of Jovanovic for pure gases has been discussed in a previous work [11]. An extension of this model to competitive binary adsorption can be derived by following the procedure reported by Jaroniec et al. [21,22] and developed later by Quinones [23]. The method is considered rigorous if a linear correlation exists between the adsorption energies of the components in the mixture. The extension is represented by the following equation:

$$Q_i = Q_{max,i} \left[1 - exp\left(\sum_{j=1}^N -b_j f_j\right)^{\overline{n}} \right]$$
(5)

The lateral-interaction parameter \overline{n} is taken as the arithmetic mean of the parameters for all of the species [24] obtained from the single-component Jovanovic model [11]; their energy distributions therefore exhibit identical shapes, with a shift of their positions on the energy axis. The extension is derived in terms of a localised adsorption model with lateral interactions in the surface phase and assuming the monolayer character of this phase. In this article, in order not to confuse the Extended Jovanovic–Freundlich equation with the conventional Freundlich model, the term "Extended Jovanovic equation" will be used instead of the term "Extended Jovanovic–Freundlich equation".

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2.5. Potential Theory for Gas Mixtures

The extension of the potential theory to a multi-component system has been studied by many authors [25–28]. The results of Doon and Yang provide an analytical solution which uses the Dubinin–Astakov equation for pure-gas adsorption isotherms:

$$W_{i} = \left(W_{max,i} - \sum_{j=1}^{m} W_{j}\right) \times \left\{\frac{exp\left[-\left(\frac{A_{i}}{E_{i}}\right)^{n_{i}}\right]}{1 - exp\left[-\left(\frac{A_{i}}{E_{i}}\right)^{n_{i}}\right]}\right\}$$
(6)

where

$$\sum_{j=1}^{m} W_{j} = \sum_{i=1}^{m} \frac{exp\left[-\left(\frac{A_{i}}{E_{i}}\right)^{n_{i}}\right]}{1 - exp\left[-\left(\frac{A_{i}}{E_{i}}\right)^{n_{i}}\right]} / \left\{1 + \sum_{i=1}^{m} \frac{exp\left[-\left(\frac{A_{i}}{E_{i}}\right)^{n_{i}}\right]}{1 - exp\left[-\left(\frac{A_{i}}{E_{i}}\right)^{n_{i}}\right]}\right\}$$

The basic assumption of this model is that there is no lateral interaction between molecules of different types; the parameters of the Dubinin–Astakov equation (W_i , E_i , and n_i) of each species are therefore not affected by the presence of the other species, but the volume available for each species is reduced. The amount adsorbed is calculated by dividing the volume, W_i , by the molar volume of adsorbate [11].

2.6. Ideal Adsorbed Solution Theory (IAS)

The IAS theory is based on the thermodynamic solution and is independent of the current adsorption model. Based on a gas mixture thermodynamic analysis [29], the fundamental equation of gas mixtures is obtained:

$$R_{g}T\sum_{j=1}^{N}x_{j}\ln\left(\frac{f_{j}}{f_{j}^{0}y_{j}e^{z_{j}}x_{j}}\right) + \varnothing\left[\frac{1}{n} - \sum_{j=1}^{N}\frac{x_{j}}{n_{j}^{0}}\right] = 0$$
(7)

where, f_j^0 is the fugacity of pure compound *j* at the referent state; *n* is the number of mole per unit mass of adsorbent; and n_j^0 is the number of moles of pure *j*-th compound per unit mass at the same referent state.

Once z_i is defined as:

$$z_j = -\frac{\varnothing - \varnothing_j^0}{n_j^0 R_g T} \tag{8}$$

where \emptyset_{j}^{0} is the surface potential of the pure *j*-th compound at the referent state, one can write:

$$f_j = f_j^0 \exp(z_j) x_j \tag{9a}$$

$$\frac{1}{n} = \sum_{j=1}^{N} \frac{x_j}{n_j^{\ 0}}$$
(9b)

where x_i is the mole fraction of the adsorbed phase.

This special solution defines an ideal adsorbed solution. Myers and Prausnitz [29] proposed the special standard state for IAS—the surface potential of the mixture should be the same as the surface potential of all the pure compounds:

$$\frac{\varnothing}{R_g T} = \frac{\varnothing_i^0}{R_g T} = -\int_0^{P_i^0} \frac{n_i^0}{P_i^0} dP_i^0$$
(10)

In this case, $z_j = 0$ (defined in Equation (8)). Replacing fugacity in terms of the total pressure and the mole fraction from Equation (9a), we obtain:

$$Py_j = x_j P_j^0(\sigma) \tag{11a}$$

where σ is the reduced spreading pressure and $P_j^0(\sigma)$ is the hypothetical pressure of the pure compound.

Equation (11a,b) can be combined to yield the following equation:

$$F(\sigma) = \sum_{j=1}^{m} x_j - 1 = \sum_{j=1}^{m} \frac{Py_j}{P_j^0(\sigma)} - 1 = 0$$
(12)

$$\sigma = \frac{A\pi}{R_g T} = \int_0^{P_1^0} \frac{Q_1}{P_1} dP_1 = \int_0^{P_2^0} \frac{Q_2}{P_2} dP_2 = \dots = \int_0^{P_m^0} \frac{Q_m}{P_m} dP_m$$
(13)

The spreading pressure, π (or the reduced spreading pressure σ), can be obtained either analytically or numerically, depending on the isotherm equation used to describe the pure-compound equilibrium. In our case (pure gases), we used the equations of Langmuir, Sips, Toth, and UNILAN, the two latters being, respectively, written for single components as [28]:

$$Q = Q_{max} \frac{bf}{\left[1 + (bf)^n\right]^{1/n}}$$

and

$$Q = \frac{Q_{max}}{2n} \frac{1 + bfe^n}{1 + bfe^{-n}}$$

For the equation of Langmuir and Sips, there exists an analytical solution [29]. For the two other equations, the numerical solution of the integral in Equation (13) was developed.

Knowing the reduced spreading pressure, σ , Equation (12) can be solved numerically in respect of the hypothetical pressure of the pure compound, $P_j^0(\sigma)$, and to the mole fraction of the adsorbed phase, x_j . The total amount adsorbed can be calculated from the equation:

$$Q_T = 1 / \sum_{j=1}^m \frac{x_j}{Q_j^0}$$
(14)

where Q_j^0 is the adsorbed amount of pure compound, *j*, at the hypothetical pressure, P_j^0 , that is:

$$Q_j^0 = f\left(P_j^0\right)$$

In our case, the functional f in the equation above takes the form of the Langmuir, Sips, Toth, and UNILAN equations. The amount adsorbed contributed by compound 'j' is therefore given by:

$$Q_j = Q_T x_j \tag{15}$$

Equation (12) was solved numerically using the Newton–Raphson method for solving algebraic equations. In order to evaluate numerically the integral in Equation (13), the quadratic method was chosen. The programming environment MatLab was used to benefit from the relevant file functions and software communication links corresponding to these numerical solutions.

2.7. Fast-IAS Theory

The Fast-IAS theory was first proposed by O'Brien and Mayers [30], and was later refined by the same authors [31]. The refined version is more efficient from the computational point of view. The method essentially uses the analytical expression for the reduced

spreading pressure in terms of hypothetical compound pressure. Because the reduced spreading pressure, *z*, is the same for all the compounds, we can write:

$$z = f_i(\varphi_i)$$
 where $\varphi_i = b_i P_i^0$

Function f_i can take different analytical forms for the reduced spreading pressure according to the type of compound isotherms used. If the gas mixture contains N compounds, the equation above represents (N - 1) equations, which can be rewritten as follows:

$$f_i(\varphi_i) = f_{i+1}(\varphi_{i+1}) \quad for \ i = 1, 2, \dots, N$$
 (16)

In terms of variable φ_i , the Raoult law becomes:

$$P_i = x_i \frac{\varphi_i}{b_i} \tag{17}$$

Because the sum of the adsorbed-phase mole fraction is unity, Equation (17) can be rearranged and summed with respect to all species, leading to the following equation:

$$\sum_{i=1}^{N} \frac{P_i b_i}{\varphi_i} = 1 \tag{18}$$

This equation, together with N - 1 equations (from Equation (16)), form a set of N equations in terms of N unknown variables, φ_i . The set of Equations (16) and (18) can be rewritten in the vector form:

$$\vec{g}\left(\vec{\varphi}\right) = 0 \tag{19}$$

A solution of this set of equations was obtained by the Newton–Raphson method. Once φ_i is known, the adsorbed-phase mole fractions are calculated for the Raoult's law (Equation (19)), the total adsorbed concentration is calculated from Equation (14), and the adsorbed-component concentration is obtained from Equation (15).

The modified Fast-IAS procedure was used to obtain the solution of Equation (19). The difference between this modified method and the original one stands with the definition of Equation (19); in the modified version, g_i is defined as the difference between the function f_i and the function f_N , meaning that the spreading pressure of pure component *i* is compared with that of the last *N*-th component, whilst in the original version, g_i corresponds to the difference between two neighbouring components f_i and f_{i+1} , respectively. The Jacobian matrix is reduced to the form such that the entire last row of the reduced matrix contents of a zero element, except for the last element of that row.

Both Fast-IAS and IAS theories require numerical computation of the solution. The difference between the two theories is that the Fast-IAS one involves the solution of N variables of pure-component pressure, $\varphi_i = b_i P^0$, whilst the solution of the spreading pressure is sought in the IAS theory. Once the spreading pressure is known in the IAS theory, the hypothetical pure-component pressure can be obtained as the inverse of the integral equation [31]. Thus, the Fast-IAS theory obtains the solution of the hypothetical pressure of the pure component by a modified matrix. On the other hand, the applicability of the Fast-IAS theory is restricted to only a few equations which yield analytical expression of the reduced spreading pressure. For the other equations, the IAS theory has to be used instead. In this study, the Langmuir and O'Brien equations have been selected to implement the Fast-IAS procedure.

3. Results and Discussion

In order to test the models discussed above, the experimental data of Wu et al. [32] have been selected. The authors provided experimental results of pure hydrogen, nitrogen, and methane gas adsorption on JX101 activated carbons for temperatures ranging from 283 to 313 K. The adsorption equilibrium data of the ternary mixture (CH₄, N₂, H₂) have

been driven up to moderate pressure. Because the models used are purely predictive, the previously obtained results for the adsorption equilibrium of pure gases are needed. The numerical experiments have been carried out in the programming environment MATLAB, which develops the relevant file functions and software communication links for the mathematical models used.

The accurate calculation of the thermodynamic properties of gases (compressibility factor, density, and fugacity) determines the accuracy of further calculations. In a previous work [33], different equations of state (EOS) have been tested for their ability to describe the real behaviour of hydrogen gas; the results of these equations were compared to the experimental results obtained from the Universal Gas Encyclopaedia and to those obtained from the NIST database [34]. From this previous study, it was demonstrated that the SBWR EOS model can be chosen for calculating the gas compressibility factor, the density, and the fugacity. In the last study [11], different models for the calculation of pseudovapour pressures and molar volumes of the adsorbed phase have been compared. A critical discussion of their accuracy and precision has been made; as a result, the use of the models of Do [28] and Dubinin [35] have been recommended. In the same study, eight models for the single-component adsorption have been fitted to the experimental isotherms of pure CH_4 , N_2 , and H_2 by nonlinear regression; in the case of pure-gas adsorption, the adsorbateadsorbent interactions are more significant than the adsorbate-adsorbate interactions. The estimated parameters for each component necessary to describe the gas mixture adsorption equilibrium have been provided [11].

The experimental data for the gas mixtures proposed by Wu et al. [32] were measured at the same temperature as for pure gases but at lower pressures, namely up to 6×10^5 Pa. All the experimental conditions are given in Table 1.

Case	T [K]	$\% y_{\mathrm{CH}_4}$	y_{N_2}	$y_{\rm H_2}$
N° 1a	283	36.48	27.75	35.77
N° 1b	298	36.48	27.75	35.77
N° 1c	313	36.48	27.75	35.77
N° 2	298	52.78	23.61	23.61
N° 3	298	25.27	23.80	50.93
N° 4	298	30.19	44.93	24.89
N° 5	298	28.47	12.03	59.50

Table 1. Experimental conditions: temperature and gas content.

All the cases listed in Table 1 have been modelled but, in order to emphasise the whole range of variations, only two of them (cases N° 2 and N° 5) are presented because they respectively correspond to the lower and greater proportions of hydrogen, whose amount strongly affects the calculation accuracy of the various models. In this instance, when modelling the other cases (cases N° 1a, N° 1b, N° 1c, N° 3, and N° 4), the same trends in the calculation accuracy of the different models have been observed. Experimental data have been modelled by the extended Langmuir, Freundlich, Sips, and Jovanovic equations. The potential theory extended for gas mixtures, as well as the IAS theory and the modified Fast-IAS theory, have also been applied.

3.1. Peculiarities in the Practical Application of Some Models

3.1.1. Results and Discussion as Regards the Application of the Extended Sips Equation

The extended Sips model for an *N*-component system has been presented in Section 2.3, where the Jaroniec's extension [21] of this model has also been introduced. Both equations are tested for their capability to predict competitive adsorption equilibria. A comparison between the data calculated by the two forms of the extended Sips model and the experimental data in the conditions of case N° 2 (see Table 1) is shown in Figure 1.



Figure 1. Adsorption results for (**a**) nitrogen and (**b**) methane gases, as experimentally observed and as modelled by the Sips equations.

In the legends of Figure 1, SIPS-1 and SIPS-2 correspond to Equations (3) and (4), respectively. Figure 1 shows that the Jaroniec's extension of the Sips equation describes more inaccurately the experimental results than the classical extension of the Sips equation. The same trend is observed when modelling all the other cases from Table 1; the classical extension of the Sips equation has therefore been selected in Section 3.2.

3.1.2. Results and Discussion as Regards the Applicability of the IAS Theory

As mentioned in the previous section, the spreading pressure, π (or the reduced spreading pressure σ), can be obtained either analytically or numerically depending on the isotherm equation used to describe the pure-compound equilibrium. In this study, the equations of Langmuir, Sips, Toth, and UNILAN for pure gases have been used. A comparison in the conditions of case N° 2 (see Table 1) between the data calculated by the IAS theory, using the four mentioned models and the experimental data, is shown in Figure 2.



Figure 2. Adsorption results for (**a**) nitrogen and (**b**) methane, as experimentally observed and as obtained with the four implemented models of the IAS theory.

The indications IAS-L, IAS-S, IAS-T, and IAS-U in the legends of Figure 2 correspond to the application of the IAS theory using the Langmuir, Sips, Toth, and UNILAN equations,

respectively. Figure 2 shows that for methane and nitrogen, the implementation of the models of Langmuir and Toth in the IAS theory provides a better fit with the experimental points, with the model curves being nearly confluent. This trend is also observed in all the other cases of Table 1. It has however been found that the most accurate fit is obtained using the Toth model. Only the Toth model has therefore been used in Section 3.2.

3.1.3. Results and Discussion as Regards the Applicability of the Fast-IAS Theory

In this study, the Langmuir and O'Brien equations for pure gases have been chosen to develop the Fast-IAS procedure described in the previous section. A comparison in the conditions of case N° 2 (see Table 1) between the results of the Fast-IAS method, using the equations of Langmuir (FAST-LANG) and of O'Brien (FAST-OBMYR), and the experimental data, is shown in Figure 3.



Figure 3. Adsorption results for (**a**) nitrogen and (**b**) methane, as experimentally observed and as obtained with the two implemented models of the Fast-IAS theory.

Figure 3 shows the good agreement between experiment and modelling. The difference between the results of the Fast-IAS theory using the model either of Langmuir or of O'Brien is very small, the curves being nearly coincident. This fact is an indication of the accuracy of the Fast-IAS procedure for describing the gas mixtures adsorption equilibria. The same trend is observed for all the other cases indicated in Table 1. In Section 3.2, the Fast-IAS theory has been applied using the O'Brien equation for pure-gas adsorption isotherms.

3.2. Results for Gas Mixtures

The seven models discussed in the previous section have been used to describe the gas mixture adsorption equilibria, namely the Langmuir (LANG.), Sips (SIPS), Freundlich (FREUN.), and Jovanovic (JOV.) equations, as well as the IAS (IAS-T) and Fast-IAS (FAST) theories and the potential theory (PT). Two of the cases listed in Table 1 have been especially exploited. In the first one (case N° 2), the percentage of hydrogen in the gas mixture is the lowest (23.63%) whilst, in the second one (case N° 5), the percentage of hydrogen in the gas mixture is the highest (59.5%). A comparison can therefore be made between the accuracy of the different models in describing the adsorption equilibrium in the cases where hydrogen is present in a greater or lesser amount, which is important from the point of view of the process of separation and purification of hydrogen from gas mixtures.

3.2.1. Modelling Results for Case $N^\circ\,2$

Figure 4a–c show a comparison between experiment and modelling corresponding to the conditions of case N° 2 in Table 1.



Figure 4. Cont.



Figure 4. (a). Adsorption results of hydrogen gas from mixture corresponding to case N° 2; (b). Adsorption results of nitrogen gas from mixture corresponding to case N° 2; (c) Adsorption results of methane gas from mixture corresponding to case N° 2.

Figure 4a depicts the model curves and the experimental data for the adsorption of hydrogen from the gas mixture. The figure shows that the experimental points are better described by the extended Freundlich model, followed by the extended Jovanovic equation, which gives larger deviations from experimental data for high pressures. All the other models do not describe the adsorption equilibrium of hydrogen with a reasonable accuracy.

Figure 4b shows the model curves and the experimental data for the adsorption of nitrogen from the gas mixture. In this case, the most accurate result has been obtained by using the extended Langmuir model followed by the extended Jovanovic equation. A reasonable accuracy has also been obtained by modelling with Fast-IAS, IAS, and PT. The extended Sips equation provided slightly lower values than the experimental ones, and the extended Freundlich equation proved inadequate, giving much higher values for the adsorption equilibrium than the experimentally observed ones.

Figure 4c shows the data for the adsorption equilibrium of methane. In this case, the experimental results are most accurately described by the PT, followed by Fast-IAS, IAS, and the extended Langmuir model. Lower values than the experimental ones have been obtained with the extended Jovanovic equation, whilst much lower and higher values have been observed with the extended Sips and Freundlich equations, respectively.

3.2.2. Modelling Results for Case N° 5

Figure 5a–c show a comparison between experiment and modelling corresponding to the conditions of case N° 5 in Table 1.



Figure 5. Cont.



Figure 5. (a) Adsorption results of hydrogen gas from mixture corresponding to case N° 5; (b) Adsorption results of nitrogen gas from mixture corresponding to case N° 5; (c) Adsorption results of methane gas from mixture corresponding to case N° 5.

Figure 5a shows the results of the adsorption equilibrium of hydrogen from the gas mixture. Here, as in the previous case, the most accurate experimental points are described by the extended Freundlich model, followed by the extended Jovanovic equation, which gives more accurate values in this case than in case N° 2 (Figure 4a). All the other models do not describe the adsorption equilibrium with a reasonable accuracy, the worst one resulting from the extended Sips equation, which gives very low values in comparison with the experimental data.

Figure 5b shows a comparison between experimental data and modelling results for the adsorption equilibrium of nitrogen from the gas mixture. In this case, the most accurate results have been obtained by using the Fast-IAS theory, followed by the IAS theory and the isotherms predicted via the extended models of Jovanovic and of Langmuir. The curves for all these models are almost merging and describe very well the experimental points. The potential theory provides slightly underestimated but reasonable results, whilst the extended Sips and Freundlich equations provide clearly underestimated and unrealistically high values, respectively.

Figure 5c shows the results of the adsorption equilibrium of methane from the gas mixture. The best experimental results have been obtained by the potential theory, followed by the Fast-IAS and IAS theories, and the extended Langmuir equation. All these models describe very well the experimental points, whilst the extended Jovanovic, Freundlich, and Sips models provide underestimated, largely overestimated, and largely underestimated results, respectively.

The comparison between Figures 4 and 5 shows that, in cases N° 2 and N° 5, the modelling of the adsorption equilibria of nitrogen and of methane by the potential theory, the IAS and Fast-IAS theories, and the extended Langmuir equation is very precise and fits well with the experimental points. In both cases, the extended Jovanovic model describes the experimental results for the nitrogen adsorption very accurately, whilst the results

for methane are slightly lower than expected, whereas the models of Freundlich and of Sips prove inaccurate with higher and lower values, respectively, both for nitrogen and methane.

In both cases, when describing the adsorption equilibrium of hydrogen from gas mixtures, the extended Freundlich model gives the best results. The extended Jovanovic model also gives results with a satisfactory precision. All the other models used in this study describe the adsorption equilibrium of hydrogen with insufficient accuracy. A similar trend has been observed when modelling cases N° 1b, N° 3, and N° 4 (see Table 1). These cases differ from each other only by the difference in the concentrations of the individual components of the gas mixture. It can therefore be concluded that the concentration of hydrogen in the gas mixture does not affect the accuracy of the calculation of the adsorption equilibrium by the different models.

In cases N° 1a, N° 1b, and N° 1c, the gas mixture has the same composition, but the adsorption equilibrium has been measured at different temperatures. When modelling these cases, the same trends have been observed with the different models, which proves that temperature does not affect their accuracy.

4. Conclusions

Seven models have been used in order to describe the adsorption equilibrium of gas mixtures. Comparing the results of numerical experiments with experimental multi-component data has shown that:

- the extended Sips equation always gives lower values than those of the experimental data and describes the adsorption equilibrium of the modelled gas mixture with insufficient accuracy;
- the extended Langmuir equation along with the IAS, Fast-IAS, and PT models give almost identical values and describe well the adsorption equilibrium of nitrogen and methane. However, when using these models to describe the adsorption equilibrium of hydrogen, unrealistically low values are obtained;
- the extended Freundlich equation gives unrealistically high values for the adsorption of nitrogen and of methane, but quite precise results for the adsorption of hydrogen;
- the extended Jovanovic model gives very accurate results for the adsorption of nitrogen whereas, in the case of methane and of hydrogen, the results are less precise.

All the models used in this study, except the extended Langmuir equation, are able to describe the heterogeneity of the adsorption surface of JX101 activated carbons. However, these models, with the exception of the extended Jovanovic equation, do not take into account the lateral interactions between different types of adsorbed molecules. The total amount adsorbed also depends on the size of the molecules. Small molecules (such as hydrogen) are more likely to insert between larger adsorbed molecules (such as nitrogen). Thus, the presented models (except Sips and Freundlich) estimate accurately the adsorption equilibrium of nitrogen because of the large size of its molecules, and the lateral interactions between the adsorbed nitrogen and the other adsorbed molecules are indeed weak.

When attractive lateral interactions between adsorbed molecules of methane and of hydrogen are present, and the size of these molecules is smaller compared to nitrogen, additional amounts of them are observed.

After comparing the models used in this study, it can be stated that the extended Freundlich and Jovanovic models give the overall best results and describe well the adsorption equilibrium of hydrogen; these models are indeed more appropriate for small molecules. The other models tested in this study (except the extended Sips equation) better describe the adsorption of larger molecules (methane and nitrogen); they therefore give lower and inaccurate values for the hydrogen adsorption. **Author Contributions:** Conceptualization, C.C. and F.L.; methodology, C.C.; software, C.C.; validation, C.C., F.L. and P.L.; investigation, C.C., P.L. and F.L.; writing—original draft preparation, C.C. and F.L.; writing—review and editing, C.C., P.L. and F.L.; supervision, F.L. and C.C. All authors have read and agreed to the published version of the manuscript.

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References

- Nicoleti, G. The hydrogen option for energy: A review of technical, environmental and economic aspects. *Int. J. Hydrogen. Energ.* 1995, 20, 759–765. [CrossRef]
- Kim, H.J.; Park, K.D.; Kim, J.T.; Seo, K.J. Thermal-Structural Characteristics of Multi-Layer Vacuum-Insulated Pipe for the Transfer of Cryogenic Liquid Hydrogen. *Metals* 2022, 12, 549. [CrossRef]
- 3. Das, L.M. On-board hydrogen storage systems for automotive application. Int. J. Hydrogen. Energ. 1996, 21, 789–800. [CrossRef]
- 4. Pullumbi, P.; Brandani, F.; Brandani, S. Gas separation by adsorption: Technological drivers and opportunities for improvement. *Curr. Opin. Chem. Eng.* **2019**, *24*, 131–142. [CrossRef]
- Sayılgan, Ş.Ç.; Mobedi, M.; Ülkü, S. Effect of regeneration temperature on adsorption equilibria and mass diffusivity of zeolite 13x-water pair. *Micropor. Mesopor. Mat.* 2016, 224, 9–16. [CrossRef]
- 6. Hamid, U.; Vyawahare, P.; Tun, H.; Chen, C.C. Generalization of thermodynamic Langmuir isotherm for mixed-gas adsorption equilibria. *AIChE J.* **2022**, *68*, e17663. [CrossRef]
- Lamari, F.D.; Weinberger, B.P.; Kunowsky, M.; Levesque, D. Material design using molecular modeling for hydrogen storage. *AIChE J.* 2009, 55, 538–547. [CrossRef]
- 8. Dicko, M.; Seydou, M.; Darkrim Lamari, F.; Langlois, P.; Maurel, F.; Levesque, D. Hydrogen adsorption on graphane: An estimate using ab-initio interaction. *Int. J. Hydrogen. Energ.* **2017**, *42*, 10057–10063. [CrossRef]
- 9. Hu, X.; Do, D.D. Multicomponent adsorption kinetics of hydrocarbons onto activated carbon: Effect of adsorption equilibrium equations. *Chem. Eng. Sci.* **1992**, *47*, 1715–1725. [CrossRef]
- 10. Guiochon, G.; Golshan-Shirazi, S.; Katti, A.M. *Fundamentals of Preparative and Nonlinear Chromatography*; Academic Press: Boston, MA, USA, 1994.
- 11. Chilev, C.; Dicko, M.; Langlois, P.; Lamari, F. Modelling of single-gas adsorption isotherms. Metals 2022, 12, 1698. [CrossRef]
- 12. Martinez, G.M.; Basmadjian, D. Towards a general gas adsorption isotherm. Chem. Eng. Sci. 1996, 51, 1043–1054. [CrossRef]
- 13. Beyaz, S.; Lamari, F.D.; Weinberger, B.; Langlois, P. Nanoscale carbon material porosity effect on gas adsorption. *Int. J. Hydrogen. Energ.* **2010**, *35*, 217–224. [CrossRef]
- 14. Jakšić, O.; Spasenović, M.; Jakšić, Z.; Vasiljević-Radović, D. Monolayer Gas Adsorption on Graphene-Based Materials: Surface Density of Adsorption Sites and Adsorption Capacity. *Surfaces* **2020**, *3*, 423–432. [CrossRef]
- Dragan, G.; Kutarov, V.; Schieferstein, E.; Iorgov, A. Adsorption Hysteresis in Open Slit-like Micropores. *Molecules* 2021, 26, 5074. [CrossRef] [PubMed]
- 16. Markham, E.C.; Benton, A.F. The adsorption of gas mixtures by silica. J. Am. Chem. Soc. 1931, 53, 497–507. [CrossRef]
- 17. Hu, X.; Do, D.D. Comparing various multicomponent adsorption equilibrium models. AIChE J. 1995, 41, 1585–1592. [CrossRef]
- 18. Digiano, F.A.; Baldauf, G.; Frick, B.; Sontheimer, H. A simplified competitive equilibrium adsorption model. *Chem. Eng. Sci.* **1978**, 33, 1667–1673. [CrossRef]
- 19. Ruthven, D.M. Principle of Adsorption and Adsorption Processes; John Wiley-& Sons: New York, NY, USA, 1984.
- 20. Sips, R. On the structure of a catalyst surface. J. Chem. Phys. 1948, 16, 490–495. [CrossRef]
- 21. Jaroniec, M.; Madey, R. Physical Adsorption on Heterogeneous Solids; Elsevier: Amsterdam, The Netherlands, 1988.
- 22. Dabrowski, A.; Jaroniec, M. Effects of surface heterogeneity in adsorption from binary liquid mixtures: III. Analysis of experimental data by using Langmuir—Freundlich type equations. *J. Colloid Interface Sci.* **1980**, *73*, 475–482. [CrossRef]
- 23. Quinones, I.; Guiochon, G. Extension of a Jovanovic–Freundlich isotherm model to multicomponent adsorption on heterogeneous surfaces. J. Chromatogr. A 1998, 796, 15–40. [CrossRef]
- 24. Kapoor, A.; Ritter, J.A.; Yang, R.T. An extended Langmuir model for adsorption of gas mixtures on heterogeneous surfaces. *Langmuir* **1990**, *6*, 660–664. [CrossRef]
- 25. Bering, B.P.; Myers, A.L.; Serpinsky, V.V. Problemi inertnosti adsorbentov. Dokl. Akad. Nauk. SSSR 1970, 193, 119–122.
- 26. Doong, S.J.; Yang, R.T. A simple potential-theory model for predicting mixed-gas adsorption. *Ind. Eng. Chem. Res.* **1988**, 27, 630–635. [CrossRef]
- 27. Mehta, S.D.; Dannes, R.P. An improved potential theory method for predicting gas-mixture adsorption equilibria. *Ind. Eng. Chem. Fundam.* **1985**, *24*, 325–330. [CrossRef]
- 28. Do, D.D. Adsorption Analysis: Equilibria and Kinetics; Imperial College Press: London, UK, 1998.

- 29. Myers, A.L.; Prausnitz, J.M. Thermodynamics of mixed-gas adsorption. AICHE J. 1965, 11, 121–127. [CrossRef]
- 30. O'Brien, J.A.; Myers, A.L. Rapid calculations of multicomponent adsorption equilibria from pure isotherm data. *Ind. Eng. Chem. Process Des. Dev.* **1985**, 24, 1188–1191. [CrossRef]
- 31. O'Brien, J.A.; Myers, A.L. A comprehensive technique for equilibrium calculations in adsorbed mixtures: The generalized FastIAS method. *Ind. Eng. Chem. Res.* **1988**, *27*, 2085–2092. [CrossRef]
- 32. Wu, Q.; Zhou, L.; Wu, J.; Zhou, Y. Adsorption equilibrium of the mixture CH₄ + N₂ + H₂ on activated carbon. *J. Chem. Eng. Data* **2005**, *50*, *6*35–642. [CrossRef]
- Chilev, C.; Lamari, F.D. Hydrogen storage at low temperature and high pressure for application in automobile manufacturing. *Int. J. Hydrogen. Energ.* 2016, 41, 1744–1758. [CrossRef]
- 34. Lemmon, E.W.; McLinden, M.O.; Friend, D.G. *Thermophysical Properties of Fluid Systems, in the NIST Chemistry Webbook, Database Reference Number 69*; National Institute of Standards and Technology: Gaithersburg MD, USA, 1998. [CrossRef]
- 35. Dubinin, M.M. Modern state of the theory of gas and vapour adsorption by microporous adsorbents. *Pure Appl. Chem.* **1965**, *10*, 309–322. [CrossRef]