Applicability of molecular simulations for modelling the adsorption of the greenhouse gas CF_4 on carbons

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Abstract

Tetrafluoromethane, CF_4, is powerful greenhouse gas, and the possibility of storing it in microporous carbon has been widely studied. In this paper we show, for the first time, that the results of molecular simulations can be very helpful in the study of CF_4 adsorption. Moreover, experimental data fit to the results collected from simulations. We explain the meaning of the empirical parameters of the supercritical Dubinin–Astakhov model proposed by Ozawa and finally the meaning of the parameter *k* of the empirical relation proposed by Amankwah and Schwarz.

Key words

Tetrafluoromethane, adsorption, activated carbons, Dubinin–Astakhov model, Monte Carlo simulations

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Introduction

Perfluorocarbons, due to their high stability and low chemical reactivity have found application in microelectronics for cleaning or printing electronic circuit boards, in semiconductor industry, and also during the process of aluminum production [1,2]. The simplest perfluorocarbon, tetrafluoromethane (CF_4), is known as a particularly powerful greenhouse gas. It absorbs IR radiation more effectively than CO_2. Considering the lifetime of this gas in the atmosphere (50000 years) leads to the conclusion that during a 100 year period CF_4 is 6500 more harmful than CO_2 [1,2]. Taking this into account there have been many attempts to find a simple and effective method of CF_4 storage. Some methods used for this purpose are based on the application of adsorption phenomena, and among adsorbents a crucial role has been played by activated carbons [1,2].

It is well known that activated carbons are widely used for the adsorption of pollutants from gaseous as well as from liquid phases [4-7]. Experimental studies reporting CF_4 adsorption data on carbons usually present only isotherms, and/or sometimes a comparison is presented with adsorption of other adsorbates [8-11]. There are however, exceptions. For example Jagiełło et al. [9] considered the possibility of using CF4 for determining the pore size distribution of activated carbons. However, generally, there is a lack of literature data reporting systematic experimental studies on CF_4 adsorption on carbons with gradually changed porosity.

The major purpose of this study is to assess the applicability of molecular simulations for prediction of carbon adsorption properties towards the powerful greenhouse gas CF_4. Its storage was studied recently using Monte Carlo simulation technique [1,2] however, the results published in the literature were limited only to slit-like micropores and to ideal carbon nanotubes. Therefore, there are no theoretical studies in the literature on CF_4 storage on realistic carbon models. This is regrettable, given that realistic models take into account pore connectivity, heterogeneity, disordered carbon structure etc., i.e. fundamental properties of real carbons.

Among realistic carbon structures the Virtual Porous Carbon (VPC) models are the most important [12-15]. Among the major advantages of VPC application we mention well defined porosity and defined chemical composition of carbon surface layer. Thus, contrary to experiment, we know everything about our VPC sample. Additionally, by a simple geometric manipulation we can easily change the porosity of VPC in a systematic way [15].

Another important consideration is that since in real carbons there is an interrelation between the porosity and the chemical composition of the carbon surface layer, it is very hard

to obtain a series of samples with progressively changed porosity. On the other hand, this is very simple for the case of VPC models. This is why in the present study we collected experimental data of CF_4 adsorption on commercially available carbons and additionally, we performed theoretical description of them. Next using a series of VPC, based on models proposed by Harris *et al*. [16-22] and Monte Carlo simulations we explore the general relationships between theoretical parameters of widely used Dubinin–Astakhov (DA) adsorption model [23-26] and carbon CF_4 storage properties. Experimental data fit quiet well to simulation results. Our relations can be very useful for predicting effective CF_4 adsorbents. Moreover, we show for the first time for CF_4, that the empirical parameter k of the supercritical version of the DA model is strictly related to the pore diameter of the activated carbon sample.

Methodology

Experimental data of CF_4 adsorption on commercial carbons

The data for CF_4 adsorption on commercial carbons are tabulated in the literature. We used the data published by Ahn et al. ($T = 303$, 323 and 343 K; this carbon is labelled in our study as AC) [11] and three sets of data published by Jagiełło et al. [8] for carbon molecular sieve Carbosieve G ($T = 258$, 275 and 296 K) and activated carbons Westvaco ($T = 268$, 283 and 297 K) and Maxsorb ($T = 268$, 283 and 296 K). The sets of adsorption isotherms were described by the supercritical version of the DA adsorption isotherm equation [26]:

$$a(p,T) = a_0(T) \times \exp\left[-\left(\frac{A(p,T)}{E} \right)^n \right] \qquad (1)$$

where a_0 is the maximum adsorption (limited by the volume of pores), E is the characteristic energy of adsorption (formally the product of the characteristic energy and the affinity coefficient), n is the best fit parameter related to the heterogeneity of an adsorbent, and A is the adsorption potential defined as:

$$A(p,T) = RT \times \ln \frac{p_s^*}{p} \qquad (2)$$

where R is the universal gas constant and p_s^* is the apparent saturated vapour pressure for supercritical conditions, calculated by the relation proposed by Amankwah and Schwarz [27]:

$$p_s^* = p_C \times \left(\frac{T}{T_C} \right)^k \tag{3}$$

where $p_C = 3.75$ MPa and $T_C = 227.51$ K are the critical parameters of CF_4, and k is the value characterising an adsorption system. The temperature dependence of maximum adsorption was estimated using the relation proposed by Ozawa *et al.* [28]:

$$a_0(T) = a_0^B \times \exp\left[-\alpha(T - T_B) \right] \tag{4}$$

where a_0^B is the value of maximum adsorption at the boiling point $T_B = 145.10$ K, and $\alpha = 0.0025$ 1/K is the thermal expansion coefficient of an adsorbate.

In order to describe the data sets by the DA model (eqs. (1)-(4)), we used the genetic algorithm proposed by Storn and Price [29], applied by us recently for the description of different datasets (see for example [25,26,30-33]). We used exactly the same procedure as described in [26]. The best fit parameters were a_0^B, E, n and k. The goodness of the fit for each isotherm was checked using the value of determination coefficient:

$$DC_T = 1 - \eta_T \tag{5}$$

where:

$$\eta_T = \frac{\sum_i \left(a_{\exp,i} - a_{theo,i} \right)^2}{\sum_i \left(a_{\exp,i} - a_{\exp,av} \right)^2} \tag{6}$$

$a_{exp,i}$ and $a_{theo,i}$ denote the experimental (or simulated – see below) and theoretical adsorption values for i-th adsorption point, respectively, and $a_{exp,av}$ is the average experimental (or

simulated) adsorption value. The global fitting parameter for a branch of isotherms is defined as:

$$DC = 1 - \sqrt{\frac{\sum\limits_{T} \eta_T^2}{3}} \qquad (7)$$

where 3 in denominator denotes the number of temperature values. The procedure of standard deviation of the best fit parameters calculation is described in Supplementary data.

Molecular Simulation

We used a series of VPC described in [34] (selected examples are shown in Fig. 1).The starting structure was S0 (see Fig. 1) composed of fullerene-like fragments (the model proposed by Harris et al.). Additional structures were created by a random incorporation of small carbon fragments. In this way we obtained a series of 10 VPC models with systematically changed porosity (we labelled the structures as: S0, S4, S8, S12, S16, S20, S24, S28, S32, S35). All VPC models were placed in cubic simulation boxes ($4.6 \times 4.6 \times 4.6$ nm) with periodic boundary conditions in all three dimensions.

The porosity of VPCs was described using the procedure proposed by Bhattacharya and Gubbins (BG) [35]. During the calculation, for each structure a uniform grid ($100 \times 100 \times 100$) of points was generated in the box. For each point (located in a pore), the largest sphere containing this point and situated in the pore was found in an iterative way (for details see for example [36,37]). Its diameter corresponds with the size of the pore containing the point. The collection of the data for all the points makes it possible to determine the histogram of pore sizes (i.e. the probabilities of finding the pores having the given effective diameter (d_{eff}) – $P(d_{eff})$). The integral curves connected with the histograms were also calculated [37]:

$$P_{int}\left(d_{eff}\right) = \sum_{d \leq d_{eff}} P(d) \qquad (8)$$

The $P_{int}(d_{eff})$ value provides the information what percentage of pores has a diameter not larger than d_{eff}. The obtained histograms were also used to calculate the average pore diameter of pores accessible for CF_4 molecules ($d_{eff,ecc,av}$):

$$d_{eff,acc,av} = \frac{\sum_{d_{eff} \geq 0.47 \; nm} d_{eff} \times P\left(d_{eff}\right)}{\sum_{d_{eff} \geq 0.47 \; nm} P\left(d_{eff}\right)} \qquad (9)$$

The lower diameter of pores assumed by us (0.47 nm) reflects the collision diameter of CF_4 molecule (see below).

Adsorption isotherms were simulated using the method proposed by Yan and de Pablo and called hyper parallel tempering Monte Carlo (HPTMC) [38]. For each VPC we used 123 replicas for temperature 283, 298 and 313 K, respectively, and the values of pressure from ca. 1 Pa up to ca. 6 MPa. The HPTMC simulations utilized 1×10^7 cycles (one cycle = 100 attempts of the change of each replica state by (i) creation, (ii) annihilation or (iii) displacement of a randomly chosen atom with equal probabilities, and one attempt of a configuration swap between a pair of randomly chosen replicas). The first 2×10^6 cycles were discarded to guarantee equilibration.

Each CF_4 molecule and each carbon atom building the VPCs were modelled as a simple Lennard-Jones (LJ) centre [39]. The potential energy of interactions was calculated using the truncated LJ potential [39]. The following values of collision diameters (σ) and potential well depth (ε) were used for CF_4: $\sigma_{ff} = 0.47$ nm, $\varepsilon_{ff}/k_B = 152.27$ K (k_B − is the Boltzmann constant) [1], and for C atoms: $\sigma_{ss} = 0.34$ nm, $\varepsilon_{ss}/k_B = 28$ K [40]. Lorentz-Berthelot rule was used for the calculation of parameters for mixed interactions [39].For each type of interactions, the cut-off distance was assumed as equal to $4.5 \times \sigma_{ij}$.

The average number of Ar atoms in each replica ($\langle N \rangle$) corresponds to the adsorption amount. We calculated the absolute adsorption per unit of carbon mass:

$$a_{abs} = \frac{\langle N \rangle}{N_C \times M_C} \qquad (10)$$

where N_C is the number of carbon atoms in a given VPC structure, and M_C is the molar mass of carbon. Adsorption excess (a_{exc}) was calculated from:

$$a_{exc} = \frac{\langle N \rangle - \rho_{bulk} \times V_{acc}}{N_C \times M_C} \qquad (11)$$

where ρ_{bulk} is the density of gaseous CF_4 for given p and T, and V_{acc} is the volume of pores accessible for CF_4 in a given VPC structure. V_{acc} was computed using Monte Carlo integration. The size of pores (limiting their accessibility) was determined analogously as in the above described BG method. In order to illustrate the degree of filling of pores accessible for the adsorbate, the CF_4 density in pores was also calculated:

$$\rho = \frac{\langle N \rangle}{N_{Av} \times V_{acc}} \qquad (12)$$

where N_{Av} is the Avogadro's number. The isosteric enthalpy of adsorption (q^{st}) was calculated from the theory of fluctuations.

Simulated adsorption isotherms were described using the DA model (eqs. (1)-(4)) and the same procedure was applied as used for the description of experimental data.

Results and discussion

Fig. 2 shows histograms of pore diameters for the studied VPC structures, and the integral pore size distribution curves. All structures are microporous, and one can observe systematic changes in porosity from the structure S0 up to S35. The changes are caused by progressive filling of larger pores by carbon fragments during an MC creation of new structures [34]. One can also see that with the progressive filling of structure S0 by carbon fragments the volume of pores accessible for CF_4 molecules decreases (see dashed line in Fig. 2).

Fig. 3 shows the results of the GCMC simulation (for $T = 298$ K; however, for the remaining temperatures similar regularities are observed). One can observe a systematic decrease in absolute and excess adsorption values with the decrease in average pore diameter. This is the result of the internal VPC structure, i.e. the decrease in pore volume and the rise in the mass of carbon with the rise in microporosity. The observed decrease in a_{exc} for larger pressures is caused by smaller rise in adsorbed amount than the increase in density of gaseous CF_4.

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If one considers the changes in density of adsorbed molecules (Fig. 3c and d) the opposite effect is observed i.e. the density increases in the opposite direction to adsorption, and this is caused by the increasing potential energy with the decrease in pore diameters. This is especially seen on the relative adsorption and adsorption enthalpy plots (Fig. 3e and f).

The influence of porosity on adsorption isotherms and energetics of the process is the smallest at low pressures. At small fillings CF_4 molecules are adsorbed inside curved fragments of the fullerene-like structure. Next, at larger pressures, during adsorption on low energetic sites (and during the filling of the whole pore space) one can observe the effect caused by the rise in adsorption potential in smaller pores. Therefore, in smaller pores the volume is utilized by molecules more efficiently, and the pressure necessary to reach a given density decreases from S0 down to the S35 VPC structure (Fig. 3d).

The results of fitting experimental and selected simulated data sets by the DA model (eqs. (1)-(4)) are presented in Fig. 4 and values obtained for the best-fit parameters are collected in Tab. 1. One can observe an excellent goodness of the fit for the experimental as well as simulated data.

The regularities observed on simulated adsorption isotherms are reflected by the values of parameters obtained from the fitting. As one can see from Tab. 1 the decrease in adsorption capacity (limited by the pore volume) from S0 down to S35 structure leads to the decrease in the value of a_0^B parameter. The decrease in pore diameter leads to a larger characteristic energy of adsorption, at the same time we observe the decrease in the maximum adsorption value. Different types of relationships between E_0 and pore diameter have been proposed in the literature for adsorbed subcritical and supercritical gases. The simplest of them are inverse relations (see for example [34] and references therein). However, there are no reports showing this type of relations for CF_4 adsorption.

As one can observe in Fig. S1 in Supplementary data the data obtained from simulations performed in this study lead to the inverse - type relationship between the both values. Moreover, from this relationship knowing the experimental value of E_0 one can easily to estimate the pore diameter from experimental data.

As one can also see k and n depend almost linearly on the reverse effective pore diameter of the studied carbon. This is very important, that the empirical parameter of Amankwah and Schwarz relation (eq. (3)) is strictly related with the average diameter of carbon micropores. It is very significant that the experimental data fit well our simulation results. If we compare the simulation with experiment we can see that for the AC carbon

having, according to the producers, an average pore diameter of 0.59 nm [11] the values of E and n (10.89 kJ/mol and 2.07, respectively) are slightly larger than observed for the VPC structure S35 (10.762 kJ/mol and 1.848, respectively), having the smallest average pore diameter (i.e. 0.661 nm). Similar E and n values as for carbon AC are observed for Carbosieve G (E = 10.863 kJ/mol, n = 2.106, see Tab. 1), therefore in this case we can expect similar pore diameter as for the AC carbon i.e. similar and equal to 0.56 nm [41]. In contrast, for the two remaining adsorbents (Westvaco and Maxsorb) the pore diameters submitted in the literature are considerably larger (Tab. 1) and this is the reason of considerably smaller E and n values, since the pore size distribution in this case should be wider.

In Fig. 5 we collect all the data considered in this study. As can be observed there is a quite good agreement between simulation and experiment. The data collected in Fig. 5 explain the experimental observation, and allows us to predict the adsorption properties towards CF_4 for other carbons. Slightly worse relation between n and inverse pore diameter is probably caused by the fact that n, as the heterogeneity measure, should be rather correlated with the width of the pore size distribution. The values of k parameter for experimental data do not fit the simulation results. This is the reason why we omitted this in the manuscript. It is obvious that simple, nanometric scale model of carbon is not a model of real sample studied experimentally. But as it can concluded from obtained results it is a good approach of the real structure.

As it was widely accepted in literature so-called DA plots (i.e. the plots of the isotherms in the linear coordinates of the DA equation) can be useful for the discussion of the mechanism of adsorption. Since the parameter n for all studied systems was calculated by us (see Tab.1) we can easily construct DA plots and they are collected in Figs. S2 and S3 (Supplementary data). Considering the DA plots for selected simulation data (Fig. S2) one can see that they are bimodal i.e. they are composed of two straight lines. The plots become more linear with the rise in temperature and with the rise in the number of small micropores in the system. Thus we can state that the mechanism of primary and secondary micropore filling occurs. In contrast, for experimental data (Fig. S3) apparently we observe the linearity of DA plots. This can be in our opinion caused by the lack of experimental points measured at higher pressures.

As one can easily see, the most promising CF_4 adsorbent should possess micropores with a diameter around 0.5 nm, and the diameters should be as homogeneous as possible (i.e. n should be larger than 2). However, more importantly, there are linear relationships between the empirical parameters of modified DA equation and micropore diameters. Moreover, the

same linear relationship occurs between k and average pore diameter. In this way, systematic computer simulation studies help to assign the meaning of the empirical parameters.

Conclusions

The results of this study show that molecular simulations are very powerful for the investigation of adsorption of the greenhouse gas CF_4 on carbons. We show for the first time, that the application of VPC models leads to results which are in good agreement with experimental data available in the literature. Experimental data fitted general correlations obtained from Monte Carlo simulations. Importantly, we show not only the general relationships but we are able, for the first time, to explain the physical meaning of the parameters of the empirical DA adsorption isotherm equation. Thus, we show that these parameters are related to the average micropore diameter of the studied carbons.

Our results also lead to the conclusion that the supercritical version of DA model proposed by Ozawa is very powerful tool and should be successful applied for the description of experimental data. Since in the current study we related the empirical parameters of the DA model (used with the empirical Amankwah and Schwarz relation to description of CF_4 adsorption data) with the parameters of carbon structure we hope that the results of this study will shed new light on the regularities observed during adsorption of this greenhouse gas.

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Table 1. The values of the best-fit parameters obtained using DA model (eqs. (1)-(4)) to description of the experimental (a) and simulated data (b). The average pore diameters are also presented (taken from the literature for real carbon samples and calculated from eq. (9) for VPCs)

Carbon	d_{av} [nm]	a_0^B [mmol/g]	E [kJ/mol]	n	k	DC_T [*)]	DC
(a) experimental data							
AC	0.59 [11]	3.09±0.35	10.89±0.56	2.07±0.15	2.75±0.17	0.9935; 0.9977; 0.9886	0.9923
Carbosieve G	0.56 [41]	8.30±0.11	10.863±0.073	2.106±0.022	4.611±0.039	0.9996; 0.9996; 0.9997	0.9996
Westvaco	1.873 [42]	7.1±1.2	7.12±0.12	1.66±0.11	2.70±0.12	0.9967; 0.9951; 0.9968	0.9961
Maxsorb	2.12 [43]	18.34±0.43	6.266±0.086	1.473±0.016	2.960±0.024	0.9998; 1.0000; 0.9998	0.9999
(b) simulated data							
S0	1.197	16.598±0.022	7.387±0.019	1.3930±0.0046	2.451±0.029	0.9999; 1.0000; 1.0000	1.0000
S4	1.000	15.291±0.025	7.970±0.030	1.5387±0.0075	2.571±0.044	0.9999; 0.9999; 0.9999	0.9999
S8	0.888	13.858±0.022	8.632±0.038	1.666±0.010	2.643±0.055	0.9999; 0.9999; 0.9999	0.9999
S12	0.823	12.434±0.019	9.208±0.041	1.736±0.011	2.699±0.060	0.9999; 0.9999; 0.9999	0.9999
S16	0.782	11.021±0.017	9.679±0.046	1.782±0.012	2.738±0.067	0.9998; 0;9999; 0.9999	0.9999
S20	0.745	10.319±0.016	9.997±0.051	1.819±0.013	2.768±0.074	0.9998; 0.9999; 0.9999	0.9999
S24	0.713	9.594±0.015	10.230±0.051	1.822±0.014	2.799±0.076	0.9998; 0.9999; 0.9999	0.9999
S28	0.689	8.964±0.015	10.478±0.056	1.845±0.013	2.835±0.081	0.9998; 0.9999; 0.9999	0.9999
S32	0.673	8.311±0.013	10.663±0.053	1.833±0.013	2.932±0.077	0.9998; 0.9999; 0.9999	0.9999
S35	0.661	7.844±0.013	10.762±0.057	1.848±0.014	3.001±0.083	0.9998; 0.9999; 0.9999	0.9999

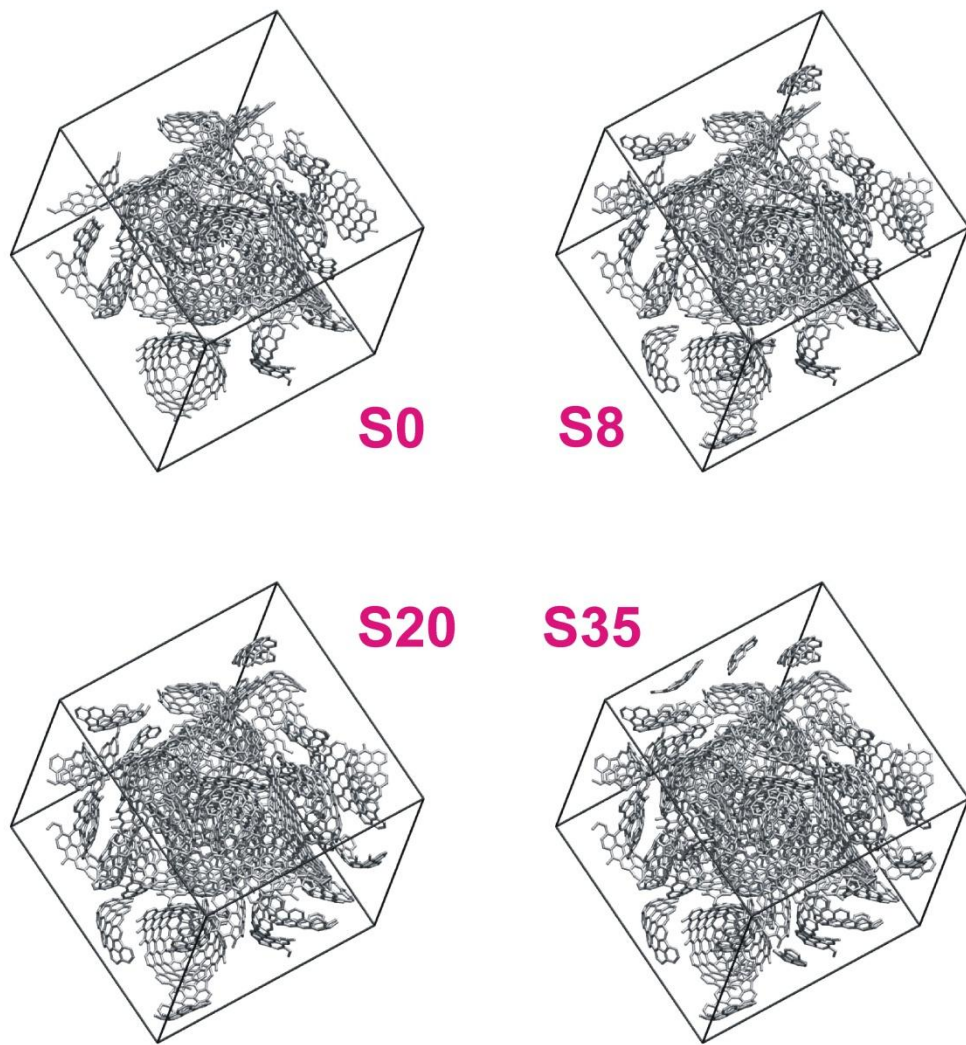[*)] – the values arranged according to the rise in temperature

Figure 1. The structure of selected VPC samples (frames reflect the size of the simulation box).
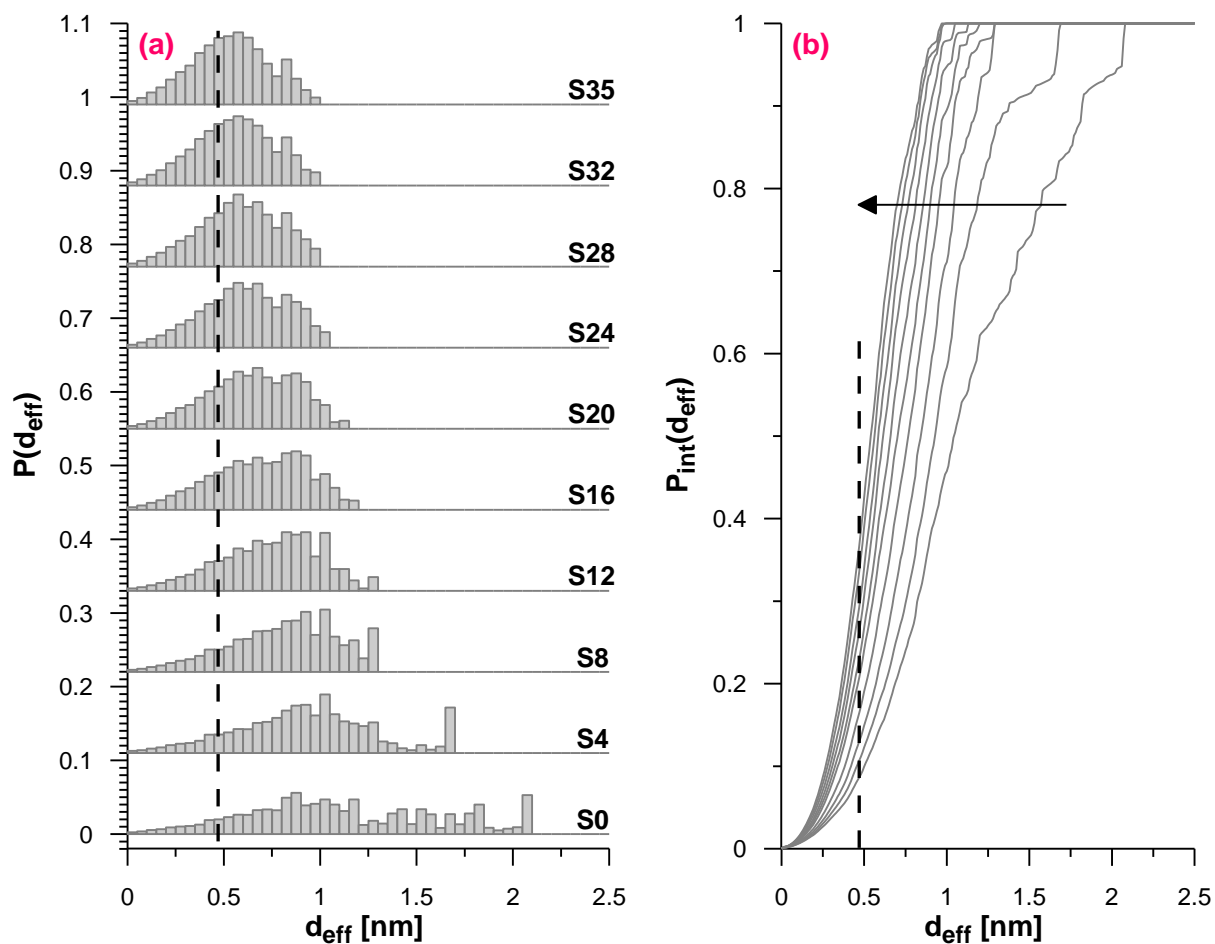
Figure 2. (a) Histograms of pore diameters for virtual porous carbons (dashed line represents the collision diameter of CF_4 molecule). (b) The integral curves related to the histograms (the arrow shows the direction of changes from structure S0 up to S35).
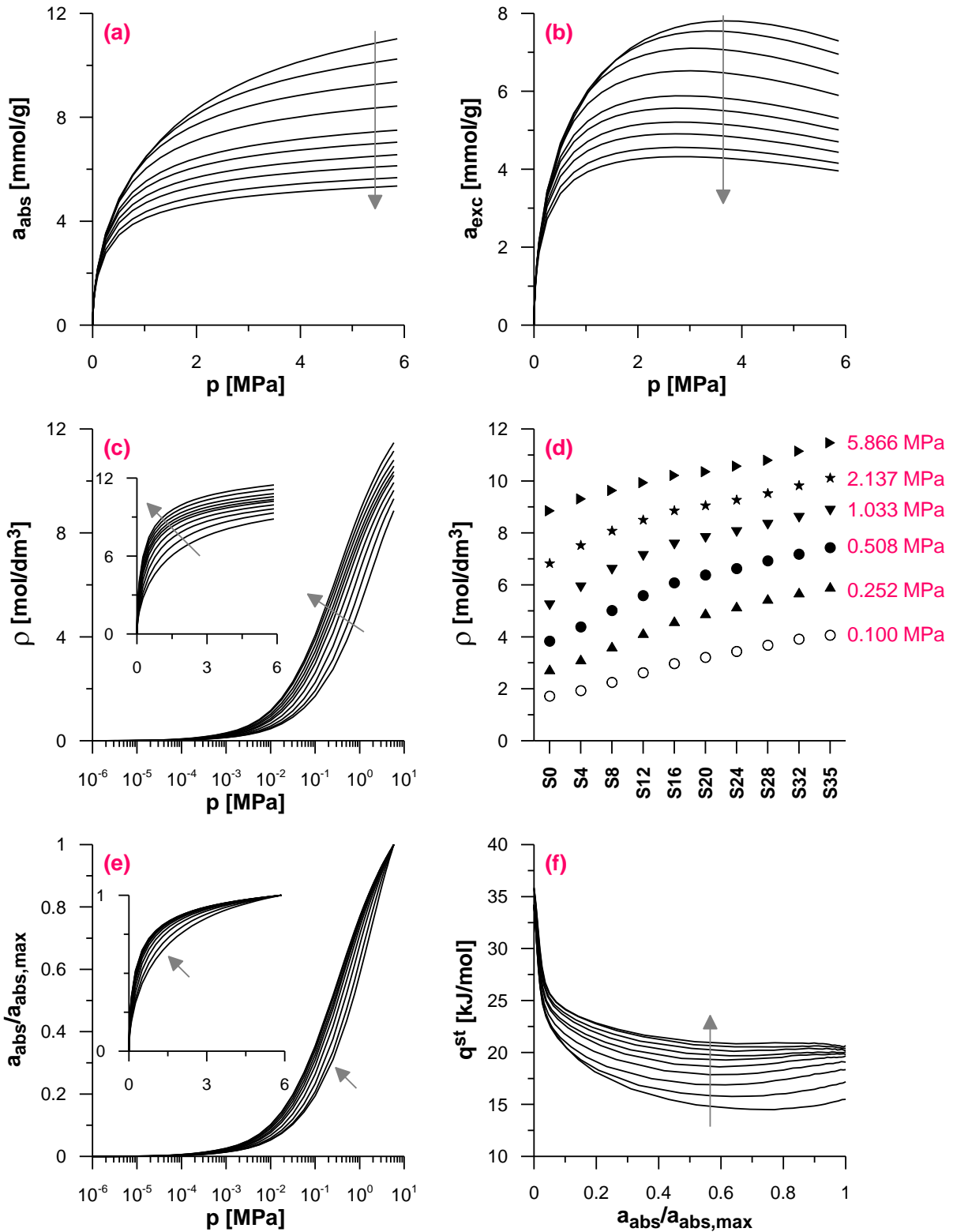
Figure 3. Comparison of simulation results for $T = 298$ K. (a) absolute adsorption, (b) excess adsorption, (c) CF_4 density in pores, (d) comparison of densities in pores for selected pressures, (e) relative adsorption, (f) isosteric adsorption enthalpy plots. The arrows show the direction of changes from structure S0 up to S35.
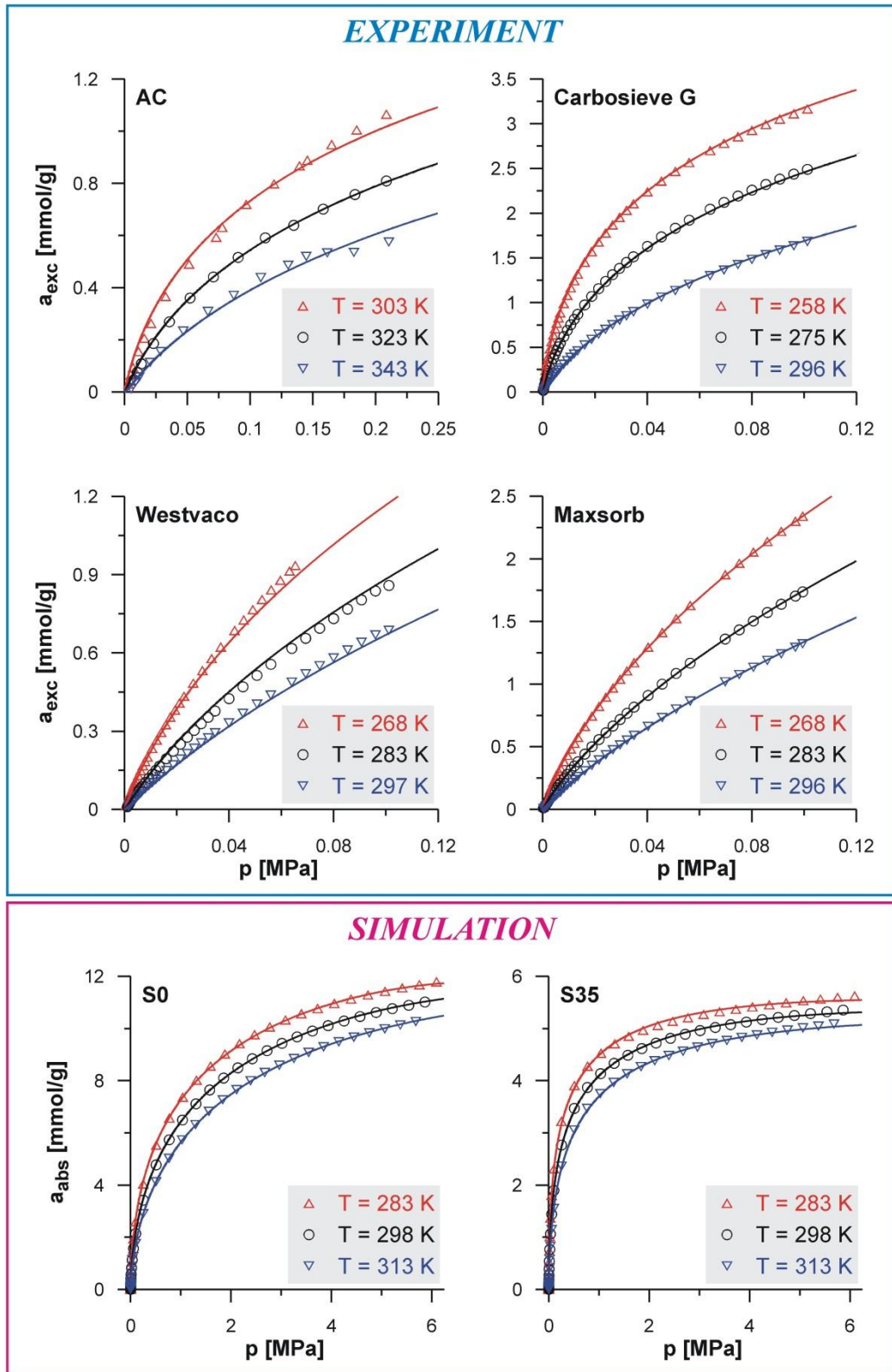
Figure 4. Graphical representation of the fitting of experimental adsorption and selected simulation isotherms using the DA model (eqs. (1)-(4)). Points – experimental and/or simulation data, lines – the model.
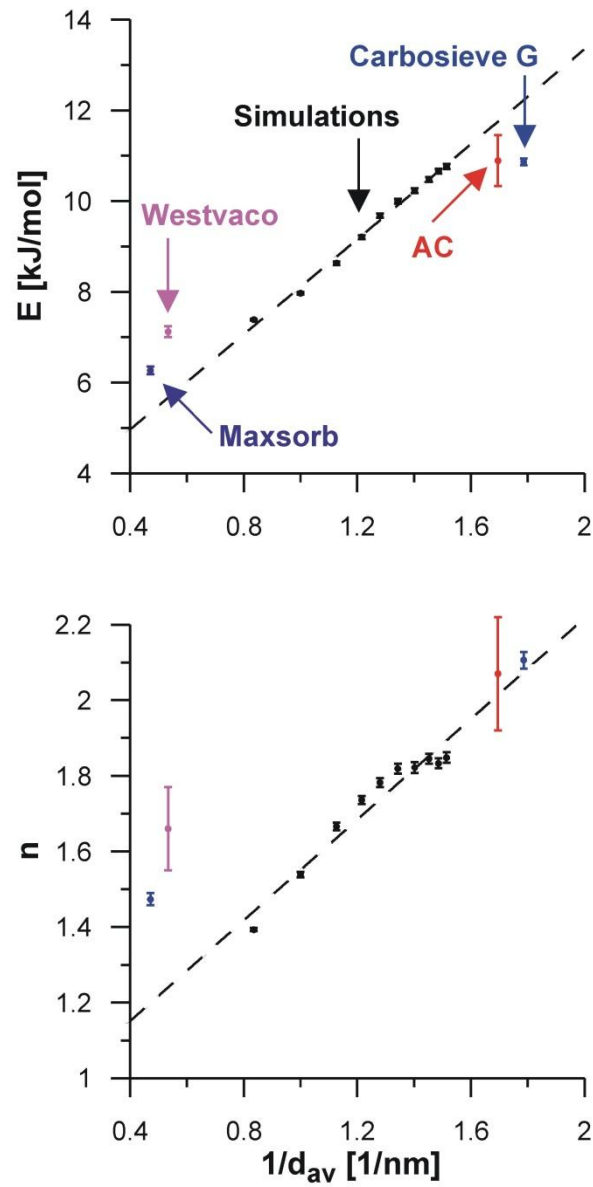
Figure 5. Comparison of characteristic energy an *n* values for experimental and simulated data (Tab. 1) as a function of reciprocals of the average pore diameters (*d*$_{av}$).