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Theoretical Description of the Calorimetric Effects Accompanying Mixed-Gas Adsorption Equilibria: Non-Symmetrical Dubinin-Astakhov Energy Distribution Function

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Possibilities of Integral Equation (IE) Approach to study the mixed-gas adsorption equilibria are considered. Generalization of Dubinin-Astakhov equation for the case of mixed-gas adsorption is presented and the corresponding expressions for isosteric heats of adsorption are obtained, taking into account the interactions between adsorbed molecules. To predict phase diagrams and isosteric heats of mixture components only the knowledge of single-gas isotherm adsorption and accompanying calorimetric effects are required. A special attention is given to possibilities of arriving at relatively simple analytical or combined analytical/numerical solutions.

Key words: adsorption, isotherms, enthalpic effects, isosteric heats of adsorption, heterogeneity

When a low productivity is needed, gas separation by adsorption processes proves to be effective. For example, in the case of oxygen or nitrogen production from air, presently it is more economical to use adsorption processes in gas separation for production rates below about 30 metric tons per day [1]. Industrial processes using adsorption phenomena involve soft technological regimes being less energy consuming. They frequently lead also to a better separation of gases.

Since experimental determination of mixed-gas adsorption data is elaborate and time-consuming, it is desirable to predict mixed-gas adsorption equilibria from the single gas adsorption isotherms. In literature a number of methods for these calculations can be found [2–31]. We propose one more model of calculations, which makes it possible to predict mixed-gas adsorption isotherms and enthalpic effects from the single gas adsorption isotherms. Recently [30,31,32] we proposed a model based on the Integral Equation Approach and Gaussian-like adsorption energy distribution. Here, we focus our attention on still another, well-known Dubinin-Astakhov (DA) energy distribution function. DA isotherm equation and its extension for the mixed-gas adsorption has already been presented by Rudzinski [8]. We present the extensions of the DA equations given earlier [8], taking into account the interactions between the adsorbed molecules. Next, we present analytical expressions for isosteric heats of adsorption in gaseous mixture corresponding to DA isotherms.

INTEGRAL REPRESENTATION FOR EQUILIBRIUM ADSORPTION ISOTHERMS

The Integral Equation (IE) approach was introduced [2] at the beginning of the seventies, being one of approaches to predict adsorption from a multi-component gas mixture onto a heterogeneous solid surface, when individual adsorption isotherms of pure components are known. In this paper the theoretical analysis of the experimental data presented will be based on localized adsorption. This will be the Langmuir model of one-site occupancy adsorption and its extensions, taking into account the interactions between the adsorbed molecules.

To describe non-ideality of gas-solid interactions the symmetrical, Gaussian-like adsorption energy distribution function is frequently used. While using that function and as local isotherm the Langmuir equation it is easy to obtain the well-known Langmuir-Freundlich equation. That case was frequently discussed [8,29]. Here we use another energy distribution function, known as the Dubinin-Astakhov function:

$$\chi_i(\varepsilon_i) = \frac{r_i(\varepsilon_i - \varepsilon_i^l)^{r_i - 1}}{(E_i)^{r_i}} \exp\left\{ -\left[\frac{\varepsilon_i - \varepsilon_i^l}{E_i} \right]^{r_i} \right\} \tag{1}$$

the variance of which is equal to E. The ε^l is the lowest value of the adsorption energy ε on a given heterogeneous surface. Depending on the shape parameter r, it is a pretty Gaussian-like function for $r = 3$, right hand widened for $r < 3$, and left hand widened for $r > 3$. When $r = 1$ DA function (1) changes to the exponential energy distribution function. Figure 2 shows the influence of the values of parameters E, r and ε^l on the shape of the function $\chi_i(\varepsilon_i)$.

Single-gas adsorption isotherms. The most frequently used method in IE approach is Condensation Approximation (CA). The simple extension of our theoretical consideration for interacting molecules is based on the Bragg-Williams isotherm equation. CA leads to the following generalization of the Dubinin-Astakhov isotherm for the single-component adsorption isotherm θ_{it}:

$$\theta_{it}(p,T) = \exp\left\{ -\left[\frac{kT}{E_i} \ln \frac{p_i^l}{p_i} - \frac{\omega_{ii}}{E_i} \theta_{it}(p,T) \right]^{r_i} \right\} \tag{2}$$

where the interaction parameter ω_{ii} is the product of the number of the nearest neighbours – adsorption sites, and the interaction energy between two molecules adsorbed on two neighbouring sites.

(2) is just the well-known Dubinin-Astakhov isotherm, or the Dubinin-Raduskevich isotherm for the particular case when $r = 2$. When $r = 1$ DA isotherm (2) becomes the Freundlich equation. Generally, r may vary from unity up to 5 or 6. It is established that $1 < r < 2$ refers to carbons with large micropores. For molecular sieves the value is 2, while very fine pore carbons and zeolites may require values up to 5 or 6 [25,26].

Thus, it is clear that the heterogeneity parameter r is related in some way to the pore dimensions. It can be shown [27], that r also depends on the analyzed region of adsorptive pressures.

The parameter p^l is commonly assumed to be the saturated vapour pressure of the adsorbate at a temperature T. But, the present computer simulations show that the state of the adsorbate molecules in the micropores is considerably different from that of the molecules in the bulk liquid. The critical temperature in the micropores is much lower, so the "micropore filling" cannot be identified with bulk condensation. Thus, p^l cannot be identified generally with the saturated vapour pressure value.

The property of parameters r and kT / E was discussed earlier, they play a role of heterogeneity parameters.

The mixed-gas adsorption equilibria. The general strategy in IE approach to obtain the theoretical expressions for the mixed-gas adsorption isotherms is use various physical arguments. Most commonly, it is done by taking into account the correlations between the adsorption energies ε_i and $\varepsilon_{j\neq i}$, $i \neq j = 1,2,3,\ldots,n$ on different adsorption sites. Two physical situations have been considered so far: 1) the adsorption energies ε_i, $\varepsilon_{j\neq i}$ are not correlated at all and, 2) a functional relationship exists.

So, for a given adsorption energy distribution function we can obtain different equations corresponding to the accepted model of correlations between adsorption energies of various components. As the first step, we consider the model of lack of correlations. This is the case of coadsorption of components exhibiting much different character of interactions with the same solid surface. We use the idea proposed by Wojciechowski *et al.* [23].

$$\theta_{it}(\{p\},T) = \left(1 - \sum_{j\neq i}^{n} \theta_{jt}\right) \aleph_i(\varepsilon_i^c) \tag{3}$$

(3) is a kind of a master equation from which various expressions for the mixed-gas isotherm can be derived by assuming various adsorption energy distributions. ($\aleph_i(\varepsilon_i)$ is the integral representation of $\chi_i(\varepsilon_i)$). The generalizations of (2) for the case of mixed-gas adsorption were published recently [32]. But, for the reader's convenience, we present briefly our theoretical considerations. To describe the interactions between the adsorbed mixture of gases we use regular adsorbed solution formalism. This approach is based on the following relation:

$$W_{ij} = \omega_{ii} + \omega_{jj} - 2\omega_{ij} = 0 \tag{4}$$

where the interchange energy W_{ij} equals zero for "ideal solution" and it is different from zero when the adsorbed mixture exhibits a non-ideal behaviour. To take into account the interactions between the adsorbed molecules we use here the Mean Field Approximation. Then, application of the Condensation Approximation for the case of random surface topography leads to the following expression for θ_{it} (the case of lack of correlations between energies of adsorbed molecules):

$$\theta_{1t}(p_1,p_2,T)=\frac{\exp\left\{-\left[\frac{kT}{E_1}\ln\frac{p_1^l}{p_1}-\sum_i\frac{\omega_{1i}\theta_{it}}{E_1}\right]^{r_1}\right\}\left(1-\exp\left\{-\left[\frac{kT}{E_2}\ln\frac{p_2^l}{p_2}-\sum_i\frac{\omega_{2i}\theta_{it}}{E_2}\right]^{r_2}\right\}\right)}{1-\exp\left\{-\left[\frac{kT}{E_1}\ln\frac{p_1^l}{p_1}-\sum_i\frac{\omega_{1i}\theta_{it}}{E_1}\right]^{r_1}-\left[\frac{kT}{E_2}\ln\frac{p_2^l}{p_2}-\sum_i\frac{\omega_{2i}\theta_{it}}{E_2}\right]^{r_2}\right\}}\tag{5}$$

For the case of high correlations between energies of adsorbed molecules of mixture, *i.e.* when the differential distribution functions $\chi_i(\varepsilon_i)$ (1) have similar shape, we obtain the following expression:

$$\theta_{it}(p,T)=\frac{(p_i/p_i^l)\exp\left\{\sum_j\frac{\omega_{ij}\theta_{jt}}{kT}\right\}}{\sum_{j=1}^{n}\left[(p_j/p_j^l)\exp\left\{\sum_k\frac{\omega_{kj}\theta_{kt}}{kT}\right\}\right]}\exp\left\{-\left[\frac{kT}{E_i}\ln\left(\frac{1}{\sum_{j=1}^{n}\left[(p_j/p_j^l)\exp\left\{\sum_k\frac{\omega_{kj}\theta_{kt}}{kT}\right\}\right]}\right)\right]^{r_i}\right\}\tag{6}$$

It can be seen that when the interaction parameters ω_{ii} are equal to zero, (5) and (6) reduce for the case of non-interacting molecules [8].

It is important to remark that to calculate mixed-gas adsorption isotherms only the best-fit parameters obtained from adjustment of DA (2) to the single-gas adsorption isotherms are required. So, assuming the ideal solution of the adsorbed phase, *i.e.* $W_{ij}=0$ (see (4)) to calculate theoretical phase diagrams no additional parameters are needed, except those obtained from adjustment by DA (2) to the single-gas adsorption isotherms. Reduction of the number of best-fit parameters simplifies our theoretical model and affects numerical calculations rate.

ISOSTERIC HEATS OF ADSORPTION

It is well known that the calorimetric effects of adsorption give more valuable information about the adsorption system than the isotherm of adsorption. For example, the heat of adsorption profile reveals the degree of energetic heterogeneity of gas-solid interactions. An increase in heat of adsorption with gas loading is characteristic for nonheterogeneous adsorbents with the constant gas-solid energies of interaction. The increase is due to cooperative interactions between the adsorbed molecules. A decrease in heat of adsorption with gas loading is characteristic for highly heterogeneous adsorbents with a wide distribution of gas-solid interaction energies. A constant heat of adsorption with gas loading indicates a balance between the strength of cooperative gas-gas interactions and the degree of heterogeneity of gas-solid interactions.

In order to apply isotherm equations to calculate the isosteric heats of adsorption we use the following well-known relations:

$$q_i^{st} = -k\left[\frac{\partial \ln p_i}{\partial(1/T)}\right]_{\theta_{it}}, \text{ or } Q_i^{st} = -k\left[\frac{\partial \ln p_i}{\partial(1/T)}\right]_{\theta_{it},\theta_{jt}}, j \neq i \tag{7}$$

where q_i^{st} and Q_i^{st} mean the isosteric heats for single and mixed-gas adsorption systems, respectively.

Based on the equations presented above, it is easy to obtain the expression describing calorimetric effects of adsorption when one component is adsorbed. When we assume DA adsorption energy distribution function (1), and use isotherm equation (2),

$$q_i^{st} = q_i^{stl} + E_i\left[\ln\frac{1}{\theta_{it}}\right]^{\frac{1}{r_i}} + \omega_{ii}\theta_{it} = q_i^{stl} - kT\ln\left(\frac{p_i}{p_i^l}\right) + \omega_{ii}\theta_{it} \tag{8}$$

where

$$q_i^{stl} = -k\frac{d\ln p_i^l}{d(1/T)} \tag{9}$$

Here, for some reasons we show the form of the theoretical isosteric heat of adsorption calculated for the case of symmetrical, Gaussian-like adsorption energy distribution [30]:

$$q_i^{st} = q_i^{st0} - c_i\ln\frac{\theta_{it}}{1-\theta_{it}} = q_i^{st0} - kT\ln(K_i^{'}p_i) \tag{10}$$

where

$$q_i^{st0} = k\frac{d\ln K_i^{'}}{d(1/T)}, \text{ and } K_i^{'} = K_i\exp\{\varepsilon_i^0/kT\} \text{ } (K_i \text{ is the Langmuir constant}) \tag{11}$$

Now, we show how to obtain theoretical expressions for isosteric heats of mixed-gas adsorption corresponding to the isotherm equations presented in this paper. Theoretical description of calorimetric effects accompanying the mixed-gas adsorption equilibria for the case of Gaussian-like adsorption energy distributions was precisely investigated in [30,31]. Theoretical studies on calorimetric effects accompanying mixed-gas adsorption, when energy distribution function is represented by the Dubinin-Astakhov eq. (1) has not been made yet.

It can be stated that the simplest method, which can be used to obtain the expressions for isosteric heats of mixture components, is the transformation of the adequate isotherm expressions for $\ln p_i$. However, it is not easy in many cases. If the transformation is not possible, the following general method can be used. Namely, the differentiation of isotherm equation function $\theta_{it}(p_1, p_2, p_1^l, p_2^l, T)$ of two components gives the following equation system:

$$\begin{gathered}\left(\frac{\partial\theta_{1t}}{\partial \ln p_1}\right)\left(\frac{\partial \ln p_1}{\partial(1/T)}\right)+\left(\frac{\partial\theta_{1t}}{\partial \ln p_2}\right)\left(\frac{\partial \ln p_2}{\partial(1/T)}\right)= \\ -\left[\left(\frac{\partial\theta_{1t}}{\partial \ln p_1^l}\right)\left(\frac{\partial \ln p_1^l}{\partial(1/T)}\right)+\left(\frac{\partial\theta_{1t}}{\partial \ln p_2^l}\right)\left(\frac{\partial \ln p_2^l}{\partial(1/T)}\right)+\left(\frac{\partial\theta_{1t}}{\partial(1/\mathrm{T})}\right)\right]\end{gathered} \tag{12}$$

$$\begin{gathered}\left(\frac{\partial\theta_{2t}}{\partial \ln p_1}\right)\left(\frac{\partial \ln p_1}{\partial(1/T)}\right)+\left(\frac{\partial\theta_{2t}}{\partial \ln p_2}\right)\left(\frac{\partial \ln p_2}{\partial(1/T)}\right)= \\ -\left[\left(\frac{\partial\theta_{2t}}{\partial \ln p_1^l}\right)\left(\frac{\partial \ln p_1^l}{\partial(1/T)}\right)+\left(\frac{\partial\theta_{2t}}{\partial \ln p_2^l}\right)\left(\frac{\partial \ln p_2^l}{\partial(1/T)}\right)+\left(\frac{\partial\theta_{2t}}{\partial(1/\mathrm{T})}\right)\right]\end{gathered} \tag{13}$$

where all differentials are calculated when the other variables are constant. The above equation system is simply linear with the two unknown: $(\partial \ln p_1 / \partial(1/\mathrm{T}))_{\{\theta_{it}\}}$ and $(\partial \ln p_2 / \partial(1/\mathrm{T}))_{\{\theta_{it}\}}$ which are the isosteric heats of adsorption of mixture components divided by $(-k)$.
In the above equation we assume that $(\partial \ln p_i^l / \partial(1/\mathrm{T}))$ will be the best-fit parameter which can be found from adjustment of theoretical isosteric heat of single component to the calorimetric data.

While considering the case of generalization of DA equation (5) (lack of correlations between adsorption energies) in order to obtain the expression for isosteric heats it is easier to use (3). Of course, the use of (3) leads to the same expression for isosteric heats of mixture components as the equation system (12–13). So, assuming that the expression for energy distribution function is represented by (1) we arrive at the following equation:

$$Q_1^{st} = q_1^{stl} + E_1\left[\ln\left(\frac{1-\theta_{2t}}{\theta_{1t}}\right)\right]^{\frac{1}{r_1}} + \omega_{11}\theta_{1t} + \omega_{12}\theta_{2t} \tag{14}$$

and, when the interactions between adsorbed molecules are neglected

$$Q_1^{st} = q_1^{stl} + E_1\left[\ln\left(\frac{1-\theta_{2t}}{\theta_{1t}}\right)\right]^{\frac{1}{r_1}} = q_1^{stl} - kT\ln\left(\frac{p_1}{p_1^l}\right) \tag{15}$$

(14) can be used for the case of lack of correlations between adsorption energies of mixture components. If we assume that correlations between adsorption energies exist, (adsorption energy distributions $\chi_i(\varepsilon_i)$ have a similar shape) the solution of (12–13) leads to the following expression for isosteric heats of adsorbed mixture components:

$$Q_i^{st} = q_i^{stl} - kT \ln \sum_i \left(\frac{p_i}{p_i^l} \exp\left\{ \sum_j \frac{\omega_{ij}\theta_{jt}}{kT} \right\} \right) + \omega_{11}\theta_{1t} + \omega_{12}\theta_{2t} \tag{16}$$

and, conseqently

$$Q_1^{st} = q_1^{st1} - kT \ln\left(\frac{p_1}{p_1^l} + \frac{p_2}{p_2^l} \right) \tag{17}$$

Here, it is substantial to show equations describing isosteric heats of adsorption obtained for the case of symmetrical, Gaussian-like adsorption energy distribution. Such studies were performed by us previously [30]. For the case of lack of correlations between adsorption energy distribution we obtained the following relation ($\omega_{ii} = 0$):

$$Q_1^{st} = q_1^{st0} - c_1 \ln \frac{\theta_{1t}}{1 - \theta_{1t} - \theta_{2t}} = q_1^{st0} - kT \ln(K_1^{'} p_1) \tag{18}$$

whereas for the case of high correlations

$$Q_1^{st} = q_1^{st0} - kT \ln(K_1^{'} p_1 + K_2^{'} p_2) \tag{19}$$

It is interesting to note, that the existence of high correlations between adsorption energies of mixture components is reflected by the difference under the logarithmic term of the corresponding expressions (14–19). While analyzing (17) and (19) we can expect that theoretical isosteric heats of adsorption calculated for the case of high correlations between adsorption energies should be approximately linear in a wide range of surface coverages. Also another conclusion can be drawn: for high values of partial pressures p_1 (and consequently high values of the mole fractions Y_1 and X_1 in gas and adsorbed phases, respectively), the values of theoretical isosteric heats of component 1 calculated from (15) and (17) or (18) and (19) should be similar (the second term under logarithm in (17) and (19) can be neglected).

Another important fact is that theoretical isosteric heats calculated for the case of lack of correlations between adsorption energies of mixture components have the same form as in the case of single-gas adsorption (see eqs (8) and (15)). We can draw conclusion that if there are no correlations between adsorption energies, calorimetric effects accompanying adsorption of mixture components are similar to those accompanying single-gas adsorption. The existence of correlations causes differences in behaviour of the theoretical isosteric heats of adsorption of mixture components. Of course, such a conclusion can be drawn only in the case of non-interacting molecules, which is justified because if neither correlations nor interactions exist there are no reasons for existence of the differences in heat effects accompanying adsorption of single gases and those in the adsorbed mixture. The existence of molecules of the second component in the adsorbed phase exhibits only by blocking adsorption sites for molecules of the first component.

Such a conclusion can be also formulated differently: if experimentally measured isosteric heats of adsorption of single gases and those gases in mixture have a similar shape it indicates lack of correlations between energies of adsorption of mixture components and weak interactions between adsorbed molecules.

So, while recapitulating our theoretical study we can state, that during the analysis of experimentally measured adsorption data we have isotherm equation (2) obtained for the case of single-gas adsorption and two isotherm equations (5) and (6) useful during the investigation of phase diagrams. Likewise studying calorimetric effects we can also use equations in the case of single gas adsorption (8) and two sets of equations (14), (15) and (16), (17) in the case of isosteric heats of adsorption determined for mixture components.

CORRELATION OF EXPERIMENTAL DATA

To calculate theoretical phase diagrams and theoretical isosteric heats of adsorption for the adsorbed gas mixture we need specific experimental data. Namely, all experimentally measured data for adsorption system i.e. single- and mixed-gas adsorption isotherms and isosteric heats of adsorption of pure and mixed gases must be measured at the same temperature. Unfortunately, it is not easy to find such data in literature. These requirements are satisfied by the experimental data reported by Dunne *et al.* [19–21] on silicalite: C_2H_6 at 23.31°C, CH_4 at 23.07°C, C_2H_6+CH_4 at 25.29°C; for NaX: CO_2 at 31.4°C, C_2H_6 at 32.4°C, CO_2+C_2H_6 at the two temperatures: 29.4°C and 28.94°C (Small differences between temperatures of measurements). While analyzing the isosteric heats of adsorption of these single gases adsorbed on silicalite and NaX, it can be assumed that in all cases the adsorption occurs like on homogeneous surface. For this reason we cannot use these adsorption data to examine our equations for isosteric heats of adsorption.

To elucidate the fundamental differences in the behaviour of the adsorption isosteric heats equations obtained by using the Integral Equation Approach, we use the adsorption data examined previously [32]. There are adsorption of carbon dioxide and methane on the microporous activated carbon Norit RB1 reported recently [33]. The authors report not only single-gas adsorption isotherms, but also adsorption data for their binary mixtures. These data are helpful for our theoretical study: when the single-gas adsorption isotherms become adjusted, we can calculate phase diagrams and compare with those measured experimentally. Unfortunately, the calorimetric data for this adsorption system are not accessible.

To present the quality of isotherms and phase diagrams correlation we used the following *Error* function (residual sum of squares): $Error = \Sigma(exp - theor)^2$. This fit is better when value of *Error* function is smaller.

The common method used to correlate experimental isotherms is the use of the logarithmic form of isotherm equations. But the main disadvantage of correlation of experimental isotherms by logarithmic form of isotherm equation (2) is the tendency do give overstated values of the monolayer capacity M_i or p_i^l. To eliminate this we fitted Dubinin-Astakhov equation in the form (2) directly to the experimentally measured isotherms.

The authors report the single-gas adsorption isotherms in a wide temperature range of 292 to 349 K and pressures to 0.8 MPa. In Figure 1 we present the best adjustment of the DA (2) to the reported adsorption data. Table 1 includes the best-fit parameters elucidated in this way. While analyzing statistically determined results we used χ^2 distribution and assumed the level of confidence $\alpha = 99\%$ (level of significance $\beta = 1\%$). Then, the probability that variances σ^2 lies in confidence interval $(0, z)$ can be expressed: $P(\sigma^2 \in (0, z)) = \alpha = 0.99$, where $z = Error/\chi^2_\alpha$.

In the last column of Table 1 we present the calculated z values.

Table 1. Values of the parameters obtained by applying the Dubinin-Astakhov equation (2) to the experimental isotherms of carbon dioxide and methane adsorbed on the activated carbon Norit RB1 reported by Van der Vaart and co-workers [33]. The applicability of that adjustment is demonstrated in Fig. 1.

	T [K]	p^l [MPa]	$\frac{kT}{E}$	r	M [mol/kg]	*Error*	z
CO_2	294.2	1.75	0.35	1.55	6.92	$1.97\cdot10^{-4}$	$5.89\cdot10^{-6}$
	303.1	**2.01**	**0.38**	**1.65**	**7.19**	$\mathbf{5.67\cdot10^{-2}}$	$1.85\cdot10^{-3}$
	311.2	1.63	0.41	1.43	5.87	$1.99\cdot10^{-4}$	$5.95\cdot10^{-6}$
	329.6	2.39	0.41	1.47	5.50	$8.77\cdot10^{-5}$	$2.62\cdot10^{-6}$
	348.3	3.02	0.42	1.46	5.02	$2.48\cdot10^{-4}$	$7.42\cdot10^{-6}$
CH_4	293.8	2.80	0.35	1.51	4.61	$1.69\cdot10^{-5}$	$5.06\cdot10^{-7}$
	303.0	**2.90**	**0.38**	**1.61**	**4.66**	$\mathbf{3.85\cdot10^{-3}}$	$1.32\cdot10^{-4}$
	311.5	4.25	0.36	1.57	4.66	$5.83\cdot10^{-4}$	$1.74\cdot10^{-5}$
	331.3	1.80	0.49	1.33	3.16	$3.29\cdot10^{-4}$	$9.84\cdot10^{-6}$
	350.6	1.33	0.59	1.32	2.55	$1.92\cdot10^{-3}$	$6.59\cdot10^{-5}$

The values of *Error* function as well as z show that very good agreement of DA equation (2) with experiment is found. For this reason we limit our theoretical consideration to the case of non-interacting molecules.

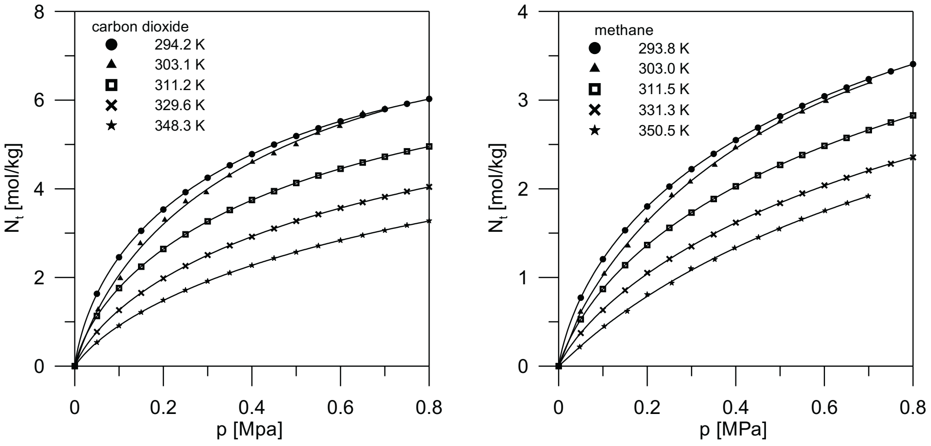

Figure 1. The single-gas adsorption isotherms of carbon dioxide and methane at the Norit RB1 activated carbon [33]. The solid lines are the theoretical isotherms calculated by using the DA isotherm equation (2) with the parameter values given in Table 1.

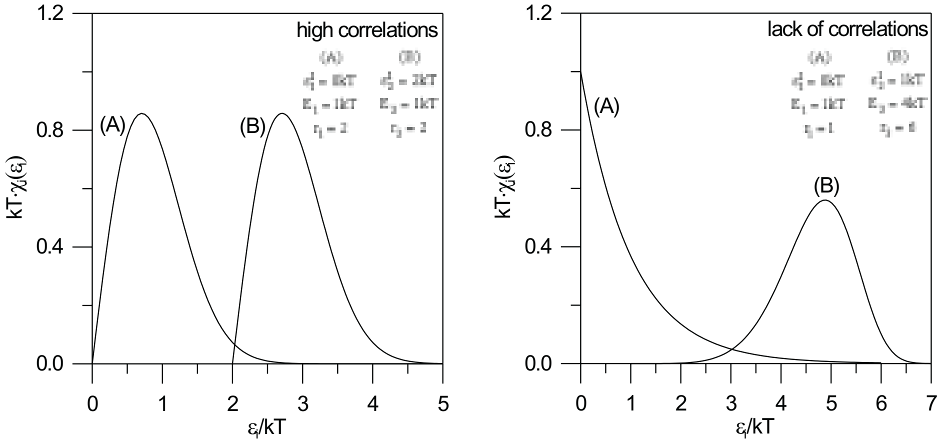

Figure 2. The existence of correlation effects between the adsorption energies of mixture components (A) and (B) described by the Dubinin-Astakhov adsorption energy distribution (1). The figure shows also the influence of the values of parameters r, E and ε^l on the shape of the function $\chi_i(\varepsilon_i)$.

Before calculating the theoretical phase diagrams for CO_2+CH_4 adsorption on activated carbon it is important to discuss the phenomenon of correlations between the adsorption energies of mixture components. Namely, the model of high correlations assumes the same shape of adsorption energy distribution function. It means that when high correlations between the adsorption energies of various components exist, the adsorption energy distribution functions are just the same, only shifted on the energy axis. Correlations between the adsorption energies of mixture components are shown graphically in Figure 2. The shape of $\chi_i(\varepsilon_i)$ functions is affected by the two parameters: r and kT/E. If we assume that high correlations between the adsorption energies of mixture components are described by relation (5), the correct use of the mixed-gas adsorption isotherm equation (6) requires the same values for r and kT/E for both mixture components. In contrast, if r and kT/E are notably different, only the model of lack of correlations should be used.

Van der Vaart *et al.* [33] reports the phase diagrams for CO_2+CH_4 measured at 302.9 K. To calculate theoretical phase diagrams we use the parameters presented in Table 1 determined from the single-gas adsorption isotherms measured at the temperatures close to the mixed-gas measurements. These parameters are marked in Table 1 by bold letters. Attentive readers can notice that, unfortunately, in the case of single-gas adsorption at the temperatures 303.1 K (CO_2) and 303.0 K (CH_4) (black triangles) the experimentally measured isotherm is charged with some experimental errors (see Figure 1). It may cause worse agreement between the theoretical and the experimental phase diagrams. While analyzing the best-fit parameters collected in Table 1, and marked by bold letters, we can see that the heterogeneity parameters kT/E and r determined for CO_2 and CH_4 single-gas adsorption are almost the same. Thus, we can use both models of correlations between adsorption energies of mixture components, *i.e.* eqs (5) and (6).

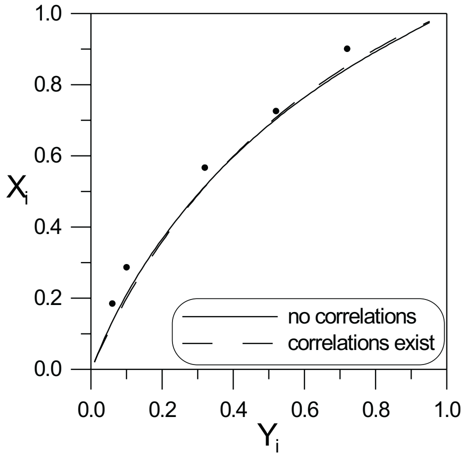

Figure 3. Adsorption from the ($CO_2 + CH_4$) gaseous mixture on the Norit RB1 activated carbon [33] at the temperature T = 302.9 K and the constant total pressure P = 0.3 MPa. Comparison with experiment (●) of the X-Y composition diagrams calculated by applying eqs. (6) (high correlations, dashed line, *Error* = $1.68 \cdot 10^{-2}$, $z = 1.11 \cdot 10^{-3}$) and (5) (lack of correlations, solid line, *Error* = $1.61 \cdot 10^{-2}$, $z = 1.06 \cdot 10^{-3}$).

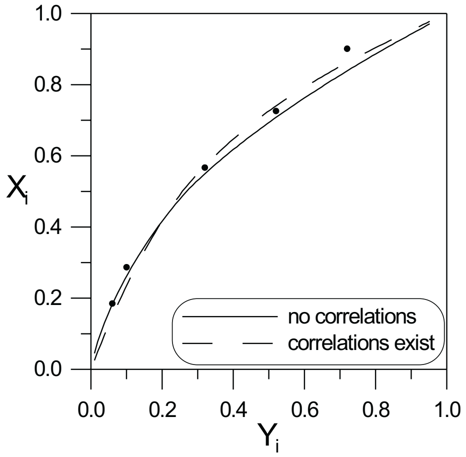

Figure 4. Adsorption from the ($CO_2 + CH_4$) gaseous mixture on the Norit RB1 activated carbon [33] at the temperature T=302.9 K and the constant total pressure P = 0.3 MPa. The lines are the theoretical phase diagrams calculated by using DA energy distribution function (1) and regular adsorbed solution theory. The values of *Error* function are following: dashed line (high correlations), *Error* = $6.85 \cdot 10^{-3}$, $z = 4.54 \cdot 10^{-4}$; solid line (lack of correlations), *Error* = $5.55 \cdot 10^{-3}$, $z = 3.68 \cdot 10^{-4}$. The Figure was taken from our recent paper [32].

The authors [33] report phase diagrams at various total constant pressures in the range to 0.8 MPa. Here we use the data obtained at the constant total pressure 0.3 MPa. In the case of other mixed-gas adsorption data at other total pressures we obtain similar results. Figure 3 shows the comparison between the theoretically calculated and the experimentally measured phase diagrams for ($CO_2 + CH_4$) adsorption on Norit RB1. It shows a similar behaviour of the models of high and lack of correlations between

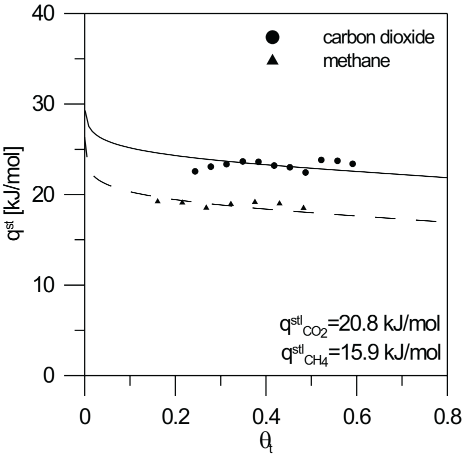

Figure 5. The isosteric heats of adsorption of pure CO_2 and CH_4 adsorbed on the Norit RB1 activated carbon [33]. The lines are the theoretical isosteric heats of adsorption calcuated by using eq. (8) with the parameter values given in Table 1. The black points are the hypothetical isosteric heats of adsorption determined from the single-gas adsorption isotherms. The values of *Error* function are following: CO_2 (solid line), $Error = 5.82$, $z = 2.35\cdot10^{-1}$; CH_4 (dashed line), $Error = 1.39$, $z = 5.62\cdot10^{-2}$.

adsorption energies of CO_2 and CH_4 molecules. But, this efficiency of calculations is not satisfactory. Recently [32] we showed, that taking into account the interactions between adsorbed molecules we obtained a better efficiency of the theoretical phase diagrams with experimentally measured (CO_2+CH_4) adsorption on Norit RB1 activated carbon. It is shown in Figure 4, where the theoretical phase diagrams were calculated by using the regular adsorbed solution theory.

Now, we begin the theoretical study of calorimetric effects accompanying CO_2 and CH_4 adsorption on Norit RB1. Unfortunately, the authors [33] did not carry out that experimental investigations. But a wide range of measured single-gas adsorption isotherms are available for us, which makes it possible to determine the hypothetical isosteric heats accompanying single-gas adsorption. The isosteric heats elucidated in this way are presented in Figure 5, where the solid lines are the isosteric heats calculated from (8). That adjustment makes it possible to determine the configurational heats q_i^{stl}. It is simply the value of isosteric heats of adsorption for the fractional coverage equal to 1. These values are presented in Figure 5 and will be helpful to calculate hypothetical isosteric heats accompanying (CO_2 + CH_4).

The course of isosteric heats of adsorption presented in Figure 5 (the heats are approximately constant with the increasing coverage) suggests the balance of transient heterogeneity and interactions between the adsorbed molecules. While taking into account the interaction effects, the theoretical isosteric heats accompanying CO_2 and CH_4 adsorption do not change in an essential way.

In Figure 6 we present the results of theoretical calculations of isosteric heats of simultaneous adsorption by using the Dubinin-Astakhov eqs (15) and (17). In the same figure we also present the theoretical isosteric heats of CO_2 and CH_4 adsorption in mixture calculated by using (18) and (19), and the values of parameters collected in Table 2. This confirms the previous conclusions that differences in theoretical isosteric heats of adsorbed mixture components are explicit for the small values of mole fraction X_i in the adsorbed phase. With the increasing values X_i of the theoretical isosteric heats calculated for the cases of lack and high correlations between adsorption energies of components mixture become the same.

Table 2. Values of the parameters obtained by applying the Langmuir-Freundlich equation to the experimental isotherms of carbon dioxide and methane adsorbed on the activated carbon Norit RB1 reported by Van der Vaart and co-workers [33].

	T [K]	$K_i \exp\{\varepsilon_i^0 / kT\}$ [1/MPa]	$\frac{kT}{c_i}$	M [mol/kg]	*Error*	z
CO_2	303.1	2.138	0.860	9.86	$5.45 \cdot 10^{-2}$	$1.78 \cdot 10^{-3}$
CH_4	303.0	1.587	0.877	6.10	$2.54 \cdot 10^{-3}$	$8.78 \cdot 10^{-5}$

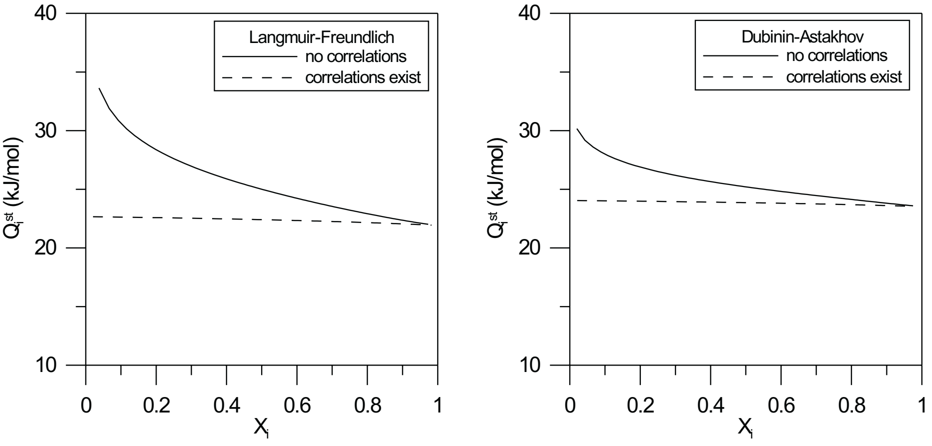

Figure 6. The hypothetical isosteric heats of simultaneous adsorption of CO_2 and CH_4 on the Norit RB1 (X_1 means the mole fraction of carbon dioxide in the adsorbed phase). The theoretical curves were calculated by applying the equations corresponding to given energy distribution functions: left figure: LF (18) (solid line, lack of correlations) and (19) (broken line, high correlations); right figure: DA (15) (solid line, lack of correlations) and (17) (broken line, high correlations).

While summarizing our theoretical study we can state that for a given model of correlations between energies of adsorption of mixture components the theoretical isosteric heats corresponding to a given adsorption energy distribution function behave similarly. While looking into Figure 6 we can carry a motion that for high values of mole fraction of a given component the differences between the models of high and lack of correlations are effaced. Also while neglecting the interaction effects between the adsorbed molecules we showed that for the case of model of lack of correlations between energies of adsorption, the expressions for isosteric heats for single- and mixed-gas adsorption of given component are just the same.

Of course, the above conclusions concerning isosteric heats of adsorption of mixture components are right only in the case when interactions between the adsorbed molecules are negligible. While analyzing the phase diagrams it can be seen from Figures 3 and 4 that taking into consideration the interaction effects between adsorbed molecules we obtained significant improvement in prediction adsorption equilibria.

The presented model of theoretical predictions of phase diagrams and enthalpic effects accompanying mixed-gas adsorption equilibria have some restrictions. The important fault is that Dubinin-Astakhov and Langmuir-Freundlich equations do not obey the Henry law. Thus, their extension to mixed-gas adsorption as well as the corresponding equations for the isosteric heat of adsorption will have very limited applicability. In addition, the DA and LF equations do not take into account different molecular sizes of components. However, the incontestable advantage of presented model of calculations is the very simple form of presented equations.

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