Adsorption 8: 45–57, 2002

On the Correct Use of the Dubinin-Astakhov Equation to Study the Mixed-Gas Adsorption Equilibria

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Abstract. This paper presents the possibilities of Integral Equation (IE) approach to study the mixed-gas adsorption equilibria. As a result, the generalizations of Dubinin-Astakhov equation for the case of mixed-gas adsorption are presented. These new equations are examined using a few adsorption systems recently published in literature.

Keywords: adsorption, isotherms, integral equation approach, heterogeneity, Dubinin-Astakhov equation

Introduction

Recently growth of interest in gas separation by adsorption processes has been observed. At the same time there appears a need for relatively simple methods to predict theoretically mixed-gas adsorption equilibria. As follows from recent literature (Rudzinski et al., 1994, 1995; Rudzinski, 1997) many methods are proposed. As the measurements of multicomponent systems are difficult and time consuming in comparison to the measurement of adsorption isotherm for pure components such theoretical predictions are important from a practical point of view.

It is well known that to obtain correct description of the adsorption phenomena the energetic heterogeneity effects must be taken into consideration. The generally accepted quantitative measure of the energetic heterogeneity of the actual solid surfaces is the differential distribution of a number of adsorption sites among the corresponding values of adsorption energy. This function is commonly called—"the adsorption energy distribution". One of the most popular theories used to describe the mixed-gas adsorption equilibria is Integral Equation (IE) Approach. Scientists using IE Approach to describe heterogeneity phenomena apply various energy distributions functions. Peculiarly Gaussian-like function is often used.

The interactions between adsorbed molecules are another important factor, which frequently plays an important role in adsorption phenomena. While taking into consideration interaction effect it is possible to obtain better description of the adsorption equilibria.

The Dubinin-Radushkevich equation is frequently used to describe adsorption on porous materials. In this paper a more general equation often called the Dubinin-Astakhov (DA) equation is used. DA equation and its extension for the mixed-gas adsorption has already been presented by prof. Rudzinski (1997). We present the extensions of the DA equations given earlier (Rudzinski, 1997) taking into account the interactions between the adsorbed molecules. To predict phase diagrams only knowledge of isotherms of single gases is required. The new isotherm and phase diagram equations are examined in a few typical adsorption systems.

The theory of gas adsorption, used by us, as one of the most common, is the Integral Equation Approach.

Integral Representation for Equilibrium Adsorption Isotherms

Let N_{it} denote the total number of the molecules adsorbed at the pressure p_i and the temperature T on a heterogeneous solid surface, and M_i denote the total number of sites on that surface. Let further

$\theta_i(\{\varepsilon\}, \{p\}, T)$ denote the "local" fractional coverage by the component i, of a certain class of adsorption sites, characterized by a set of the adsorption energies $\{\varepsilon\} = \{\varepsilon_1, \varepsilon_2, \ldots, \varepsilon_n\}$ for the single components. The experimentally monitored N_{it} value is then expressed by the following integral equation (Hoory and Prausnitz, 1967)

$$\theta_{it}(\{p\}, T) = \frac{N_{it}}{M_i} = \int_{\Omega_n} \cdots \int \theta_i(\{\varepsilon\}, \{p\}, T) \times \chi_n(\{\varepsilon\})\, d\varepsilon_1 \ldots d\varepsilon_n \tag{1}$$

where $\theta_{it}(\{p\}, T)$ is the average fraction of surface coverage by the molecules of the component i at a set of the partial pressures $\{p\} = \{p_1, p_2, \ldots\}$. $\chi_n(\{\varepsilon\})$ is the n-dimensional differential distribution of the number of the adsorption sites among various sets $\{\varepsilon\}$, normalized to unity,

$$\int_{\Omega_n} \cdots \int \chi_n(\{\varepsilon\})\, d\varepsilon_1 \ldots d\varepsilon_n = 1 \tag{2}$$

where Ω_n is the n-dimensional physical domain of $\{\varepsilon\}$.

For the adsorption isotherms of single components,

$$\theta_{it}(p, T) = \int_{\Omega_i} \theta_i(\varepsilon_i, p, T)\chi_i(\varepsilon_i)\, d\varepsilon_i \tag{3}$$

where

$$\chi_i(\varepsilon_i) = \int_{\Omega_{n-1}} \cdots \int \chi_n(\{\varepsilon\})\, d\varepsilon_1 \ldots d\varepsilon_{i-1} \cdot d\varepsilon_{i+1} \ldots d\varepsilon_n \tag{4}$$

That equation is used either to calculate $\theta_{it}(p, T)$ when $\theta_i(\varepsilon_i, p, T)$ and $\chi_i(\varepsilon_i)$ are known, or, to calculate $\chi_i(\varepsilon_i)$ when $\theta_{it}(p, T)$ and $\theta_i(\varepsilon_i, p, T)$ are known. The "local" adsorption isotherm may be Langmuir isotherm or another one (BET, Bragg-Williams, Hill-de Boer, etc.).

The really existing adsorption energy distributions are expected to have a pretty complicated form, with a number of local maxima and minima. However, to a certain degree of accuracy, the really existing function $\chi_i(\varepsilon_i)$ can, for practical purposes, be approximated by some "smoothed" functions, the shape of which is described by a small number of parameters. The following functions have, most frequently, been used to represent the "smoothed" form of the actual adsorption energy distributions:

1. The rectangular function (Myers, 1984)

$$\chi_i(\varepsilon_i) = \begin{cases} \dfrac{1}{\varepsilon_i^m - \varepsilon_i^l}, & \text{for } \varepsilon \in \left(\varepsilon_i^l - \varepsilon_i^m\right) \\ 0, & \text{elsewhere} \end{cases} \tag{5}$$

   where $(\varepsilon_i^l - \varepsilon_i^m)$ is the physical domain of ε_i.
2. The Gaussian-like function (Rudzinski and Everett, 1992)

$$\chi_i(\varepsilon_i) = \frac{\frac{1}{c_i}\exp\left\{\frac{\varepsilon_i - \varepsilon_i^0}{c_i}\right\}}{\left[1 + \exp\left\{\frac{\varepsilon_i - \varepsilon_i^0}{c_i}\right\}\right]^2} \tag{6}$$

   centered at $\varepsilon_i = \varepsilon_i^0$. For obvious physical reasons, there must be a certain minimum, and a maximum value of the adsorption energy ε_i, on a heterogeneous solid surface, ε_i^l and ε_i^m. Thus, the Gaussian-like function (6) becomes a rectangular (constant) energy distribution when $c \to \infty$.
3. The Dubinin-Astakhov function

$$\chi_i(\varepsilon_i) = \frac{r_i\left(\varepsilon_i - \varepsilon_i^l\right)^{r_i - 1}}{(E_i)^{r_i}} \exp\left\{-\left[\frac{\varepsilon_i - \varepsilon_i^l}{E_i}\right]^{r_i}\right\} \tag{7}$$

   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 (7) changes to the exponential energy distribution function.

The most frequently used method to calculate the integral in Eq. (3) is Condensation Approximation (CA). Application of the CA makes it possible to simplify the calculations. For example, if the local isotherm $\theta(\varepsilon_i, p_i, T)$ under the integral sign is the Langmuir isotherm:

$$\theta_i(\varepsilon_i, p_i, T) = \frac{K_i p_i \exp\left\{\frac{\varepsilon_i}{kT}\right\}}{1 + K_i p_i \exp\left\{\frac{\varepsilon_i}{kT}\right\}} = \frac{\exp\left\{\frac{\varepsilon_i - \varepsilon_i^c}{kT}\right\}}{1 + \exp\left\{\frac{\varepsilon_i - \varepsilon_i^c}{kT}\right\}} \tag{8}$$

where $\varepsilon_i^c = -kT\ln(K_i p_i)$. The Condensation Approximation is based on the assumption that adsorption on a heterogeneous surface proceeds in an ideally "stepwise" fashion in the sequence toward decreasing adsorption energies. It means, that the true kernel

$\theta(\varepsilon_i, p_i, T)$ in Eq. (3) is replaced by the following step function, $\theta_{ic}(\varepsilon_i, p_i, T)$

$$\theta_i(\varepsilon_i, p_i, T) \to \theta_{ic}(\varepsilon_i, p_i, T) = \begin{cases} 0, & \text{for } \varepsilon_i < \varepsilon_i^c \\ 1, & \text{for } \varepsilon_i \geq \varepsilon_i^c \end{cases} \tag{9}$$

Then,

$$\theta_{it}(\{p\}, T) = \int_{\varepsilon_i^c}^{\infty} \chi_i(\varepsilon_i)\, d\varepsilon_i = -\aleph\left(\varepsilon_i^c\right) \tag{10}$$

where $\aleph_i(\varepsilon_i)$ is the integral form of $\chi_i(\varepsilon_i)$.

The case when $\chi_i(\varepsilon_i)$ is the Gaussian-like function (6) was precisely investigated in our previous papers (Rudzinski et al., 1994; Nieszporek, 1999). Now, we focus our attention on the case when the energy distribution function is described by the non-symmetrical Dubinin-Astakhov function (7). In this case the CA approximation leads to the following expression for the fractional coverage:

$$\theta_{it}(p_i, T) = \exp\left\{-\left[\frac{kT}{E_i} \ln \frac{p_i^l}{p_i}\right]^{r_i}\right\} \tag{11}$$

Equation (11) 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 (11) 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 (Dubinin and Astakhov, 1971; Dubinin and Stoeckli, 1980). Thus, it is clear that the heterogeneity parameter r is related in some way to the pore dimensions. It can be showed (Ozawa et al., 1976), 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.

Frequently to adjust the Dubinin-Astakhov equation (11) to experimental data it is easier to use the following linear form:

$$\ln N_{it} = \ln M_i - \left[\frac{kT}{E_i}\right]^{r_i} \left[\ln \frac{p_i^l}{p_i}\right]^{r_i} \tag{12}$$

When the parameters p_i^l, r_i are correctly chosen, $\ln N_{it}$ should be the linear function of $[\ln p_i^l / p_i]^{r_i}$ in the whole range of the surface coverages.

The Mixed-Gas Adsorption Equilibria

In order to obtain the theoretical expressions for mixed-gas adsorption isotherms it is necessary to evaluate integral (1). A general strategy is to reduce this integral to a dimensional one, by using 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 $\varepsilon_i, \varepsilon_{j\neq i}$ are not correlated at all;
2. A functional relationship exists (Jaroniec and Rudzinski, 1975):

$$\varepsilon_i = f_{ij}(\varepsilon_j), \quad i \neq j = 1, 2, 3, \ldots, n. \tag{13}$$

In our theoretical model we use the adsorption energy distribution described by the Dubinin-Astakhov function, i.e. Eq. (7). Next, we assume that the local adsorption isotherm is described by the Benton equation (Markham and Benton, 1931) which is simply the generalized Langmuir equation for the case of mixed-gas adsorption isotherm:

$$\theta_i(\varepsilon_i, p_i, T) = \frac{K_i p_i \exp\left\{\frac{\varepsilon_i}{kT}\right\}}{1 + \sum_j K_j p_j \exp\left\{\frac{\varepsilon_j}{kT}\right\}} \tag{14}$$

It has been used for a long time as an empirical equation in the computer programs controlling gas separation processes. Then

$$\varepsilon_i^c = -kT \ln\left(\sum_j K_j p_j \exp\left\{\frac{\varepsilon_j}{kT}\right\}\right) \tag{15}$$

So, we can obtain two different equations dependent on 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. (1985):

$$\theta_{it}(p,T) = -\left(1 - \sum_{j\neq i}^{n} \theta_{jt}\right) \aleph_i\left(\varepsilon_i^c\right) \tag{16}$$

(16) is kind of a master equation from which various expressions for the mixed-gas isotherm can be derived by assuming various adsorption energy distributions $\chi_i(\varepsilon_i)$.

When $\chi_i(\varepsilon_i)$ is the function (7), Eq. (16) leads to the generalized Dubinin-Astakhov equation (Rudzinski, 1997):

$$\theta_{1t}(p,T) = \frac{\left[1 - \exp\left\{-\left[\frac{kT}{E_2}\ln\left(\frac{p_2^l}{p_2}\right)\right]^{r_2}\right\}\right]\exp\left\{-\left[\frac{kT}{E_1}\ln\left(\frac{p_1^l}{p_1}\right)\right]^{r_1}\right\}}{1 - \exp\left\{-\left[\frac{kT}{E_1}\ln\left(\frac{p_1^l}{p_1}\right)\right]^{r_1} - \left[\frac{kT}{E_2}\ln\left(\frac{p_2^l}{p_2}\right)\right]^{r_2}\right\}} \tag{17}$$

Let us consider the case of very high correlations between ε_i and ε_j represented by the following condition (Jaroniec et al., 1978),

$$\varepsilon_j = \varepsilon_i + \Delta_{ji}, \quad i,j = 0,1,2\ldots n \quad \text{on each adsorption site,} \tag{18}$$

where Δ_{ji}'s are certain constants. This case can be used only when the components of the adsorbed mixture have a similar chemical character. Another obvious condition is that the molecules of different components should have similar sizes. Then, if $\theta_i(\varepsilon_i, p_i, T)$ is the Benton equation (14) and $\chi_i(\varepsilon_i)$ is the DA function (7), the CA approach leads to the following form of θ_{it} (Rudzinski, 1997):

$$\theta_{it}(p,T) = \frac{p_i/p_i^l}{\sum_{j=1}^{n} p_j/p_j^l}\exp\left\{-\left[\frac{kT}{E_i}\ln\left(\frac{1}{\sum_{j=1}^{n} p_j/p_j^l}\right)\right]^{r_i}\right\} \tag{19}$$

However, even in the case of such chemically similar molecules, the functional relationship (13) may have a form more complicated than that in Eq. (18). It can be deduced from low-temperature adsorption isotherms of single components. At low temperatures, the adsorption will proceed in a fairly stepwise fashion, and the experimentally measured isotherm $\theta_{it}(p,T)$ will be given by Eq. (10). At the same coverage of surface by two components i and j, the following relation will hold (Valenzuela et al., 1989):

$$-\aleph_i\left(\varepsilon_i^c\right) = -\aleph_j\left(\varepsilon_j^c\right) \tag{20}$$

Thus in the case of Dubinin-Astakhov adsorption energy distribution (7) from Eqs. (10) and (20) we obtain the following interrelation:

$$\varepsilon_j = \varepsilon_j^l + E_j\left(\frac{\varepsilon_i - \varepsilon_i^l}{E_i}\right)^{r_i/r_j} \tag{21}$$

The Lateral Interactions between Adsorbed Molecules

The simple extension of our theoretical consideration for interacting molecules is based on the Bragg-Williams isotherm equation. The Condensation Approximation leads to the following generalization of the Dubinin-Astakhov equation:

$$\theta_{it}(p,T) = \exp\left\{-\left[\frac{kT}{E_i}\ln\frac{p_i^l}{p_i} - \frac{\omega_{ii}}{E_i}\theta_{it}(p,T)\right]^{r_i}\right\} \tag{22}$$

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.

A convenient way, frequently suggested in literature (Rudzinski, 1997), to correlate the experimental data by Eq. (22) is to use the logarithmic form,

$$\ln\theta_{it} = \ln\frac{N_{it}}{M_i} = -\left(\frac{kT}{E_i}\right)^{r_i}\left[\ln\frac{p_i^l}{p_i} - \frac{\omega_{ii}}{kT}\frac{N_{it}}{M_i}\right]^{r_i} \tag{23}$$

By choosing suitably the parameters M_i, p_i^l, ω_{ii}, r_i one should get a linear plot of $\ln(N_{it}/M_i)$ vs. the variable $[\ln p_i^l/p_i - (\omega_{ii}/kT)(N_{it}/M_i)]$. Usually the term $(\omega_{ii}/kT)(N_{it}/M_i)$ within the square bracket is a correction term compared to $\ln p_i^l/p_i$. Thus, in the first step one can find good approximate values of M_i, p_i^l, r_i, by making the plot $\ln(N_{it}/M_i)$ vs. $[\ln p_i^l/p_i]^{r_i}$ linear (simply using the results obtained for the case of non-interacting molecules). That first step should be done for the region of small adsorbate pressures, where the correction term is expected to be small. In the next step the region of higher adsorbate pressures is to be taken into analysis too, and by using the previously estimated

values of the parameters M_i, p_i^l, r_i, one has to make the plot $\ln(N_{it}/M_i)$ vs. $[\ln p_i^l/p_i - (\omega_{ii}/kT)(N_{it}/M_i)]$ linear in the whole region of pressures.

Due to a large number of best-fit parameters in Eqs. (22) or (23), the above described method is not so comfortable as it appears. The main disadvantage of correlation of experimental isotherms by the logarithmic form of isotherm equation (22) is tendency to give overstated values of the monolayer capacity M_i or p_i^l. To eliminate this we fitted Dubinin-Astakhov equation in the form (22) directly to the experimentally measured isotherms.

Next, we arrive at the generalization of our mixed-gas isotherm equations. To describe the interactions between the adsorbed mixture of gases we use regular adsorbed solution formalism. This approach is based on the following relation:

$$W_{ij} = \omega_{ii} + \omega_{jj} - 2\omega_{ij} = 0 \tag{24}$$

where the interchange energy W_{ij} is equal to zero for the case of "ideal solution" and different from zero when the adsorbed mixture exhibits non-ideal behaviour.

To take into account the interactions between the adsorbed molecules we will use here the Mean Field Approximation. Then, application of the Condensation Approximation to develop corresponding expressions for θ_{it} in the adsorbed gas-mixture (the case of random surface topography) leads to the following form of ε_i^c:

$$\varepsilon_i^c = -kT \ln K_i p_i - \sum_j \omega_{ij}\theta_{jt} \tag{25}$$

Then

$$\aleph_i\left(\varepsilon_i^c\right) = -\exp\left\{-\left(\frac{kT}{E_i}\ln\frac{p_i^l}{p_i} - \sum_j \frac{\omega_{ij}\theta_{jt}}{E_i}\right)\right\} \tag{26}$$

and, after solving equation system (16) we obtain the following equation for θ_{it} (the case of lack of correlations between energies of adsorbed molecules):

$$\theta_{1t}(p_1, p_2, T) = \frac{\exp\left\{-\left[\frac{kT}{E_1}\ln\frac{p_1^l}{p_1} - \sum_i \frac{\omega_{1i}\theta_{it}}{E_1}\right]^{r_1}\right\}\left(1 - \exp\left\{-\left[\frac{kT}{E_2}\ln\frac{p_2^l}{p_2} - \sum_i \frac{\omega_{2i}\theta_{it}}{E_2}\right]^{r_2}\right\}\right)}{1 - \exp\left\{-\left[\frac{kT}{E_1}\ln\frac{p_1^l}{p_1} - \sum_i \frac{\omega_{1i}\theta_{it}}{E_1}\right]^{r_1} - \left[\frac{kT}{E_2}\ln\frac{p_2^l}{p_2} - \sum_i \frac{\omega_{2i}\theta_{it}}{E_2}\right]^{r_2}\right\}} \tag{27}$$

For the case of high correlations between energies of adsorbed molecules of mixture, i.e. when the differential distribution functions $\chi_i(\varepsilon_i)$ (7) have similar shape we obtain the following expression:

$$\theta_{it}(p, T) = \frac{\left(p_i/p_i^l\right)\exp\left\{\sum_j \frac{\omega_{ij}\theta_{jt}}{kT}\right\}}{\sum_{j=1}^n\left[\left(p_j/p_j^l\right)\exp\left\{\sum_k \frac{\omega_{kj}\theta_{kt}}{kT}\right\}\right]}\exp\left\{-\left[\frac{kT}{E_i}\times\ln\left(\frac{1}{\sum_{j=1}^n\left[\left(p_j/p_j^l\right)\exp\left\{\sum_k \frac{\omega_{kj}\theta_{kt}}{kT}\right\}\right]}\right)\right]^{r_i}\right\} \tag{28}$$

It can be seen that when the interaction parameters ω_{ii} are equal to zero, the above Eqs. (27) and (28) reduce for the case of non-interacting molecules (17) and (19).

It is important to remark that to calculate mixed-gas adsorption isotherms only the best-fit parameters obtained from adjustment of DA Equation (22) to the single-gas adsorption isotherms are required. So, assuming the ideal solution of the adsorbed phase, i.e. $W_{ij} = 0$ (see Eq. (24)) to calculate theoretical phase diagrams no additional parameters are needed, except those obtained from adjustment by DA equation (22) to the single-gas adsorption isotherms. Reduction of the number of best-fit parameters simplifies our theoretical model and affects numerical calculations rate.

Predictions of Mixed-Gas Adsorption Equilibria

The mixed-gas isotherm equations (27) and (28) have been examined here by considering a few adsorption systems reported in literature. There are adsorption of carbon dioxide and methane on the microporous activated carbon Norit RB1 reported recently (Van der Vaart et al., 2000), ethylene and methane adsorbed on the Nuxit-A1 charcoal (Szepesy and Illes, 1963), and carbon dioxide, nitrogen and methane adsorbed on the Norit R1 Extra activated carbon (Dreisbach et al., 1999), propane and carbon dioxide adsorbed on H-mordenite (Talu and Zwiebel, 1986). Authors report not only single-gas adsorption isotherms, but also

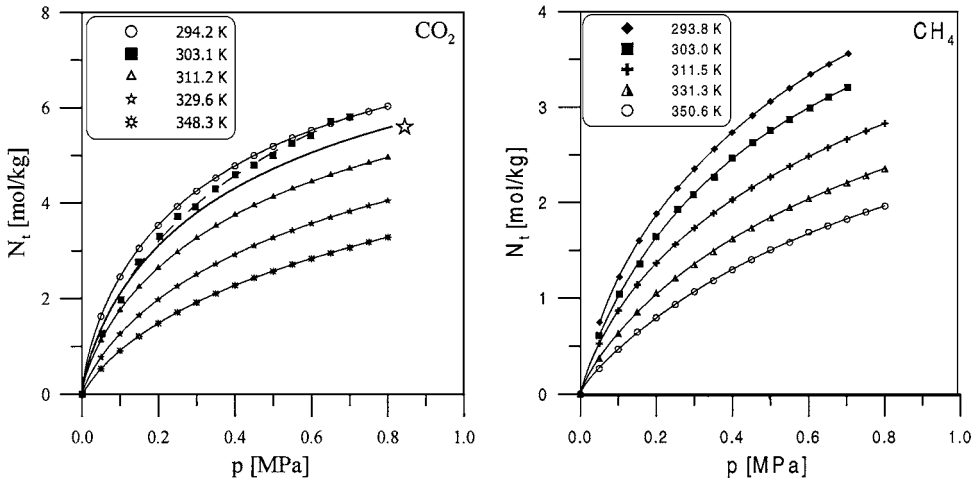


Figure 1. The single-gas adsorption isotherms of carbon dioxide and methane at the Norit RB1 activated carbon (Van der Vaart et al., 2000). The solid line is the theoretical isotherms calculated by using the DA isotherm equation (22) with the parameter values given in Table 1.

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.

To present the quality of isotherms and phase diagrams correlation we used the following *Error* function (mean residual sum of squares):

$$Error = \frac{1}{n}\sum(exp - theor)^2,$$

n—number of experimental points

This fit is better for when value of *Error* function is smaller.

As the first we investigate the adsorption system of CO_2 and CH_4 adsorbed on Norit RB1 and reported by Van der Vaart et al. (2000). 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 Fig. 1 we present the best adjustment of the generalized DA equation (22) to the reported adsorption data. Table 1 includes the best-fit parameters elucidated in this way. Very good agreement of DA equation (22) with experiment is found.

Due to a wide range of temperature of measured adsorption isotherms we can draw some conclusions. Namely, in the case of CH_4 adsorption, the monolayer capacity M decreases with growing temperature which is not a physically meaningful result. But we can state that this is a rule which appeared in many adsorption systems investigated by us previously (Nieszporek, 1999). Also the values of the parameter kT/E hold almost the same values in the whole range of temperature measurements which means that the adsorption energy distribution function becomes wider. We can also observe a regularity in behaviour of values of parameter p_i^l—the value of p_i^l increases with the growing temperature.

It can be also stated that in the case of CO_2 adsorption, the attractive interactions between the adsorbed

Table 1. Values of the parameters obtained by applying the Dubinin-Astakhov equation (22) to the experimental isotherms of carbon dioxide and methane adsorbed on the activated carbon Norit RB1 reported by Van der Vaart et al. (2000). The last column includes the values of *Error* function. The applicability of that adjustment is demonstrated in Fig. 1.

	T (K)	p^l (MPa)	$\frac{kT}{E}$	r	M (mol/kg)	$\frac{\omega}{kT}$	*Error*
CO_2	294.2	1.49	0.44	1.21	6.90	0.89	1.13×10^{-3}
	303.1	**1.77**	**0.43**	**1.34**	**7.48**	**0.33**	**9.49**
	311.2	5.32	0.36	1.36	7.50	1.17	5.29×10^{-4}
	329.6	6.14	0.35	1.52	6.72	0.55	2.34×10^{-4}
	348.3	15.4	0.29	1.88	7.42	−0.32	1.81×10^{-3}
CH_4	293.8	2.09	0.41	1.46	4.85	0.00	1.38×10^{-4}
	303.0	**4.32**	**0.39**	**1.46**	**4.99**	**0.83**	$\mathbf{4.48 \times 10^{-3}}$
	311.5	5.42	0.35	1.60	4.70	0.09	5.28×10^{-5}
	331.3	6.28	0.41	1.35	4.36	0.90	6.17×10^{-5}
	350.6	10.00	0.43	1.28	3.93	1.67	6.41×10^{-5}

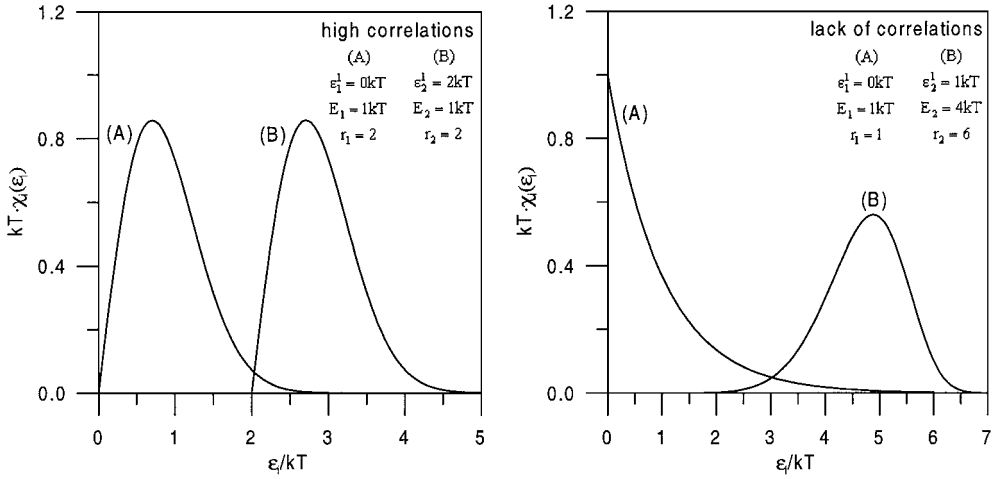


Figure 2. Existence of correlations effect between the adsorption energies of mixture components (A) and (B) described by Eq. (18). Figure shows also the influence of the values of parameters r and E on the form of the adsorption energy distribution $\chi_i(\varepsilon_i)$ calculated from Eq. (7).

molecules at the highest temperature 348.3 K change to repulsive ones. But, it is necessary to remember that the determined values of interaction parameters are certain averages, sometimes charged with some errors in measurement or numerical adjustment of theoretical isotherm equation. Some of the determined parameters in Eq. (22) can be correlated.

Attentive readers can notice that unfortunately in the case of single-gas CO_2 adsorption at the temperature 303.1 K (empty circles) the experimentally measured isotherm is charged with some experimental errors (see Fig. 1). It may cause worse agreement between theoretical and experimental phase diagrams. The existence of experimental error is confirmed by appearance of the interception of the CO_2 adsorption isotherms at temperatures 294.2 K and 303.1 K. (see Fig. 1). To eliminate this intersection we optimize the fitting parameters using the adsorption isotherms at all the temperatures collectively, i.e. correlating those isotherms altogether. So, in Fig. 1 the solid line marked by star is the expected shape of adsorption isotherm of CO_2 measured at 303.1 K.

Before calculating 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 on Fig. 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 (18), the correct use of the mixed-gas adsorption isotherm equation (28) requires the same values for r and kT/E for both mixture components. In contrast, if r and kT/E are notable different, only model of lack of correlations should be used. While calculating theoretical phase diagrams we show that even if r and kT/E estimated from single-gas adsorption isotherms are different, always better works model assuming lack of correlations between energies of adsorbed molecules.

Van der Vaart et al. (2000) reports phase diagrams for $CO_2 + CH_4$ measured at 302.9 K. To calculate theoretical phase diagrams we use parameters presented in Table 1 determined from single-gas adsorption isotherms measured at the temperatures close to the mixed-gas measurements. These parameters are marked in Table 1 by bold letters.

Van der Vaart et al. (2000) reports 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 $(CO_2 + CH_4)$

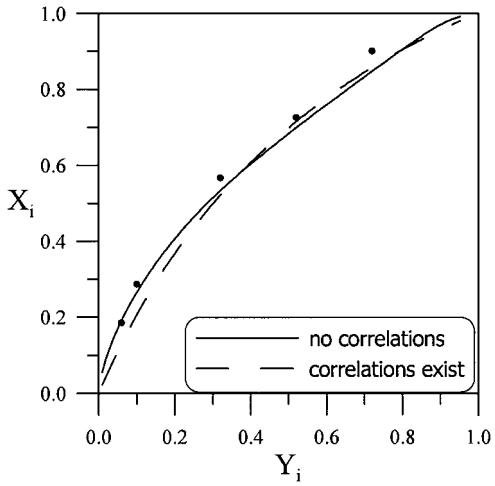


Figure 3. Adsorption from the ($CO_2 + CH_4$) gaseous mixture on the Norit RB1 activated carbon (Van der Vaart et al., 2000) at the temperature $T = 302.9$ K and the constant total pressure $P = 0.3$ MPa. Comparison with experiment (●) of the X-Y composition diagrams calculated by applying Eq. (27) (solid line, $Error = 8.60 \times 10^{-4}$) and Eq. (28) (dashed line, $Error = 2.54 \times 10^{-3}$). The calculations were performed with the assumption of ideal adsorbed phase, i.e. the interchange energy $W_{ij} = 0$.

adsorption on Norit RB1. It shows a little better efficiency of the model of lack of correlations between adsorption energies of CO_2 and CH_4 molecules. The values of r for both components are a little different.

Our consideration about correlations in the mixed-gas adsorption describe by DA Eqs. (27 and 28) is confirmed by the other adsorption systems analyzed. This is adsorption of ethylene and methane on Nuxit-AL charcoal reported by Szepesy and Illes (1963). In Fig. 4 we present both adjustment of single-gas adsorption isotherms by DA equation (22) and predicted phase diagrams. The parameters elucidated from the single-gas adsorption isotherms are collected in Table 2. We can state that the model of lack of correlations works better than that of high correlations: the values of parameters r and kT/E for ethylene and methane are different.

The third of the investigated adsorption systems are the adsorption data reported by Dreisbach et al. (1999): high pressure adsorption data of methane, nitrogen and carbon dioxide and their binary mixtures on the activated carbon Norit R1 Extra. The best-fit values obtained from adjustment of DA equation (22) to the single-gas adsorption isotherms are presented in Table 2.

While calculating phase diagrams for the adsorption systems reported by Dreisbach et al. (1999) we must explain a certain property of these adsorption data. Namely, the phase diagrams were determined at varied total pressure. Therefore we cannot calculate theoretical phase diagrams as a continuous function. Our theoretical phase diagrams are the collection of points calculated for each mole fraction of the gas phase determined during experiment.

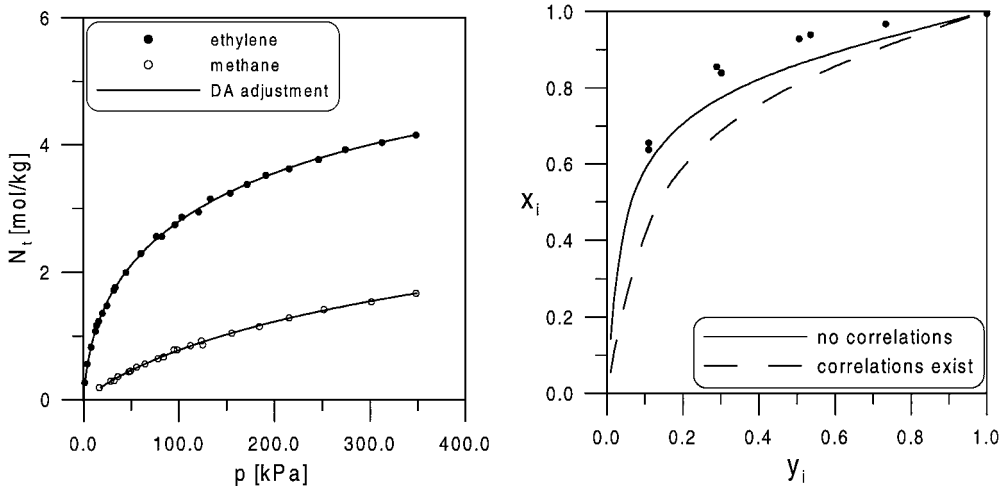


Figure 4. Single and mixed-gas adsorption of C_2H_4 and CH_4 on the Nuxit-AL charcoal (Szepesy and Illes, 1963) at the temperature $T = 293.1$ K and the constant total pressure $P = 99.2$ kPa. Comparison with experiment (●,○) of the X-Y composition diagrams calculated by applying Eq. (27) (solid line, $Error = 3.02 \times 10^{-3}$) and Eq. (28) (dashed line, $Error = 2.05 \times 10^{-2}$). The theoretical phase diagrams were calculated with the assumption $W_{ij} = 0$.

Table 2. Values of the parameters obtained by applying the Dubinin-Astakhov equation (22) to the experimental isotherms of ethylene and methane adsorbed on Nuxit-AL (Szepesy and Illes, 1963), carbon dioxide, nitrogen and methane adsorbed on the activated carbon Norit R1 Extra (Dreisbach et al., 1999) and propane and carbon dioxide adsorbed on the H-mordenite (Talu and Zwiebel, 1986). The last column includes the values of *Error* function.

		T (K)	p^l (MPa)	$\frac{kT}{E}$	r	M (mol/kg)	$\frac{\omega}{kT}$	*Error*
Nuxit-Al	C_2H_4	293.1	1.138	0.25	2.03	4.86	−1.37	7.0×10^{-4}
	CH_4	293.1	3.040	0.37	1.62	3.13	0.34	2.8×10^{-4}
Norit R1 extra	CO_2	298.0	20.000	0.176	6.64	11.318	−4.197	7.05×10^{-3}
	N_2	298.0	10.69	0.394	1.583	4.885	0.017	4.63×10^{-5}
	CH_4	298.0	10.96	0.340	1.54	7.587	0.57	1.42×10^{-3}
H-mordenite	C_3H_8	303.15	0.250	0.161	1.00	1.27	0.62	1.11×10^{-2}
	CO_2	303.15	0.298	0.310	1.21	2.75	0.53	1.68×10^{-4}

Figure 4 shows our results of prediction of phase diagrams for adsorption of (CH_4 + N_2), (CH_4 + CO_2) and ($CO_2 + N_2$) adsorbed on the activated carbon Norit R1 Extra. We observe very good agreement of DA equation (22) adjusted to the single-gas adsorption isotherms and weak conformity of predicted phase diagrams (empty symbols) with experiment. However, it can be stated that in every case the model of lack of correlations reproduces better the adsorption systems studied by Dreisbach et al. (1999). It is confirmed by different values of r and kT/E for the adsorbed mixture components (see Table 2, Fig. 5).

Finally, we decided to carry out a certain model of investigations to show how various parameters affect the X-Y diagrams of mixed-gas adsorption. Figure 6 shows the behaviour of the theoretical phase diagrams (27) and (28) in the special case when all best-fit parameters obtained from adjustment of DA equation (22) to the experimental single-gas adsorption isotherm have the same values: $r_1 = r_2 = 1.0$; $kT/E_1 = kT/E_2 = 1.0$; $M_1 = M_2 = 1.0$, $p_1^l = p_2^l = 1.0$; and the total pressure equal 0.99 MPa. Figure 6 requires some discussion. Namely, when for certain values of partial pressures of mixture components there is observed the same composition of gas and adsorbed phases, the mixture exhibits "azeotropic" behaviour. The term "azeotrope" was taken from the theories of liquid-vapour equilibria, and had there its source in non-ideality of a liquid mixture. There is, therefore, a strong tendency in adsorption literature to consider the interactions between the adsorbed molecules as the source of the azeotropes in the phase diagrams. It can be showed (Rudzinski, 1997), that surface energetic heterogeneity may affect strongly the shape of these phase diagrams, and may also be a source of the observed azeotropes. It can be also deduced from analysis of the behaviour of theoretical phase diagrams (27) and (28). For example, the azeotropic behaviour may simulate suitable selection of the heterogeneity parameters r_i and kT/E_i. Figure 6 shows that also when mixture components are similar in the physicochemical sense, the essential source of azeotropes is the lack of correlations between the adsorption energies of co-adsorbed gases (Rudzinski, 1997).

To check in practice, how the Dubinin-Astakhov multi-component isotherm equations can predict azeotropic behaviour we use the experimental data reported by Talu and Zwiebel (1986). This is adsorption of propane and carbon dioxide on H-mordenite at 303.15 K. This adsorption system exhibit azeotropic behaviour i.e. crossover in the composition diagram. The results of theoretical predictions are presented in Table 2 (values of the parameters determined from the single-gas adsorption isotherms) and in Fig. 7. This shows poor agreement of theoretical phase diagrams with the experiment. Better agreement with the experiment is achieved with the model of lack of correlations (27) (values of r and kT/E for C_3H_8 and CO_2 are different) which exhibits azeotropic behaviour of ($C_3H_8 + CO_2$) adsorption system. It seems that theoretical predictions of azeotropic behaviour by the Dubinin-Astakhov equations (27) and (28) should be treated rather qualitatively than quantitatively.

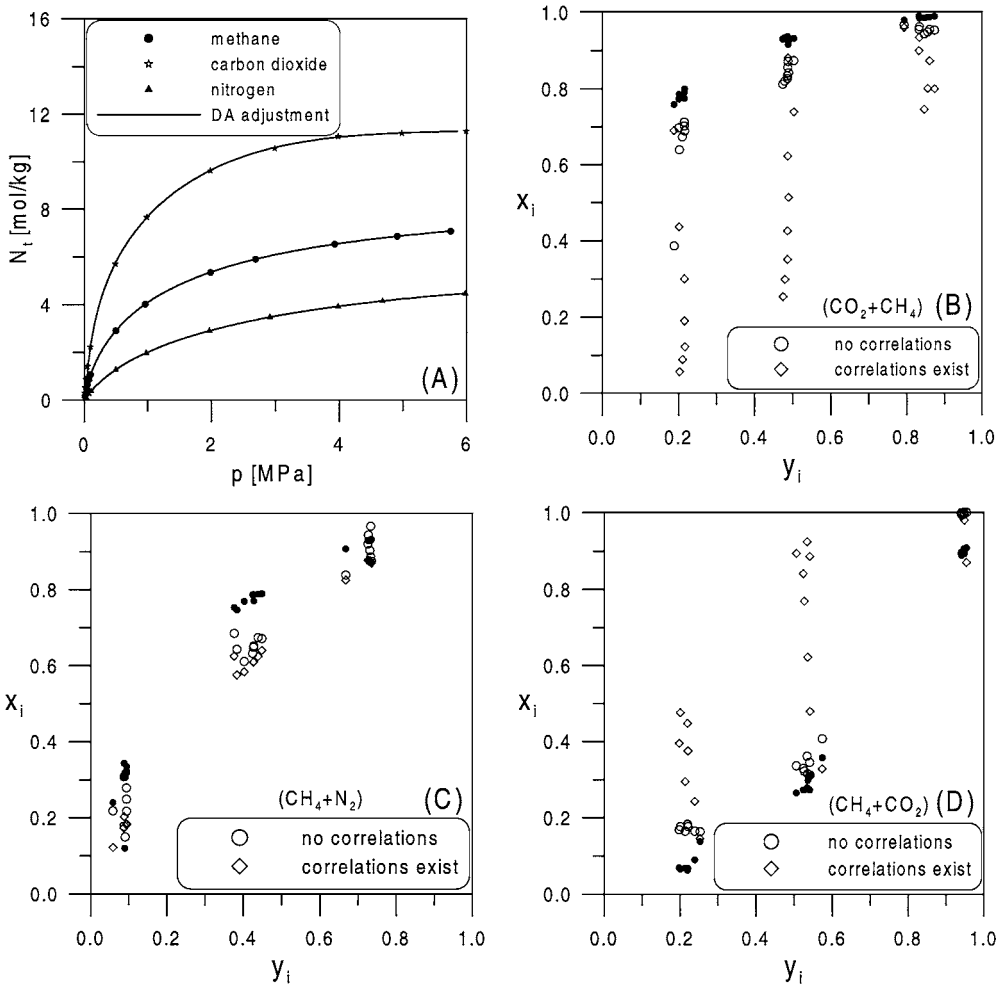


Figure 5. The adsorption of CH_4, CO_2 and N_2 on the Norit R1 extra activated carbon (Dreisbach et al., 1999) at the temperature $T = 298$ K. Part (A): the adjustment of DA equation (22) to the experimentally measured single-gas adsorption data; part (B): the mixed-gas adsorption ($CO_2 + N_2$); part (C): adsorption of ($CH_4 + N_2$) mixture; part (D): adsorption of ($CH_4 + CO_2$) gaseous mixture. Black symbols (●) indicate experimental data whereas empty symbols (○) and (◇) are the theoretically calculated phase diagrams by applying Eq. (27) (no correlations) and (28) (high correlations), respectively. The theoretical phase diagrams were calculated with the assumption $W_{ij} = 0$. The values of mean residual sum of squares *Error* are following: part (A): see Table 2; part (B): $Error^{\text{uncorr.}} = 1.23 \times 10^{-2}$, $Error^{\text{corr.}} = 1.85 \times 10^{-2}$, part (C): $Error^{\text{uncorr.}} = 8.87 \times 10^{-3}$, $Error^{\text{corr.}} = 1.39 \times 10^{-2}$, part (D): $Error^{\text{uncorr.}} = 4.54 \times 10^{-3}$, $Error^{\text{corr.}} = 1.15 \times 10^{-2}$.

In closing our numerical exercises we would like to discuss applicability of the presented isotherm equations. Namely, how it can be stated when it is sufficient to use the equations obtained for the case of non-interacting molecules. We show it by using a linear form (23) of the Dubinin-Astakhov equation (22). This Eq. (23) differs from (12) by the lateral interaction term $(\omega_{ii}/kT) \cdot (N_{ii}/M_i)$. For the case of adsorption systems in which interactions are significant, this term is simply correction to linearity. Figure 8 shows linear regression (12) for the single-gas adsorption of C_3H_8 and CO_2 on the H-mordenite (Talu and Zwiebel, 1986). The plot was drawn using the values of parameters p^l and r collected in Table 2. It shows that up to $[\ln(p^l/p)]^r = 5$ the experimental points are linear. So, for the case of C_3H_8 and CO_2 adsorbed on the H-mordenite at 303.15 K (Talu and Zwiebel, 1986) the second term in Eq. (23) can be neglected up to the pressures about 2 kPa (propane) and 6 kPa (carbon dioxide). Generally, it is not possible to state when it is sufficient to use equations neglecting interactions between the adsorbed molecules. In each

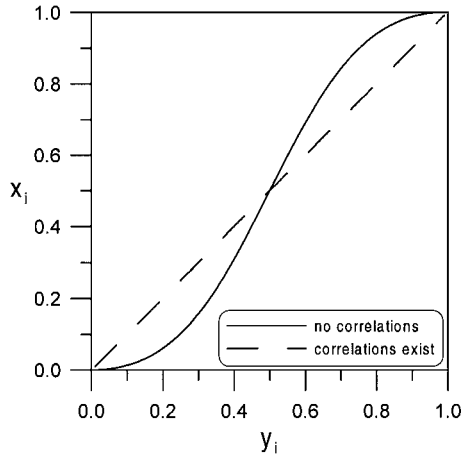


Figure 6. The theoretical phase diagrams calculated by using Eq. (17) (solid line) and Eq. (19) (broken line), when $r_1 = r_2 = 1.0$; $kT/E_1 = kT/E_2 = 1.0$; $M_1 = M_2 = 1.0$, $p_1^l = p_2^l = 1.0$, and the total pressure equal 1 MPa.

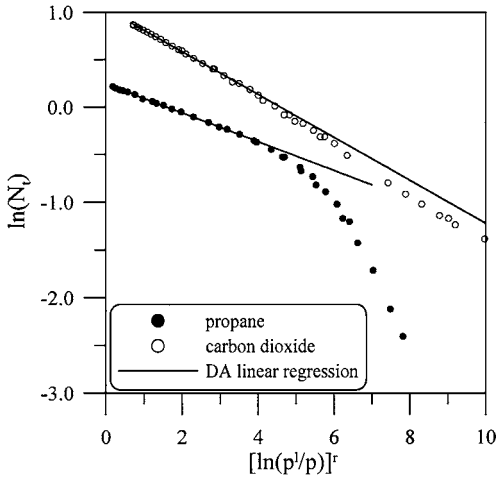
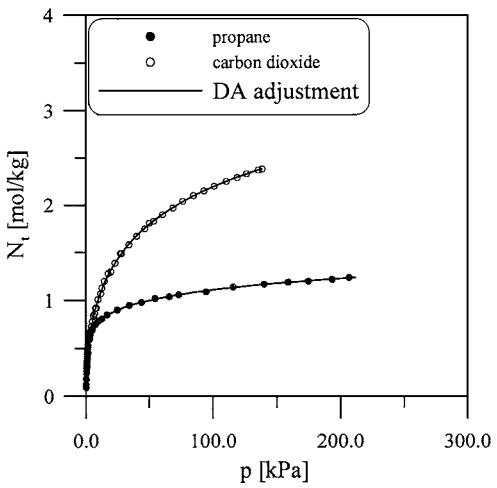


Figure 8. Linear regression (12) (solid lines) for the single-gas adsorption of C_3H_8 (●) and CO_2 (○) on the H-mordenite (Talu and Zwiebel, 1986) at the temperature $T = 303.15$ K.

case it is necessary to draw the plot $\ln N_t$ vs. $\ln p$ to check the deviation from linearity of the experimental points.

In all cases we performed our calculations assuming the interchange energy W_{ij} equal zero i.e. we assume that the adsorbed mixture exhibits ideal behaviour. For the case of non-ideal mixtures W_{ij} is one more best-fit parameter improving the theoretical adjustment of phase diagrams. In such cases W_{ij} is optimized from the experimental binary adsorption data. Such treatment has been presented recently in literature (Ritter and Al.-Muhtaseb, 1998; Al.-Muhtaseb and Ritter, 1999). But while using W_{ij} as the best-fit parameter, insignificant improvement of theoretical phase diagrams with the analyzed adsorption systems is observed.



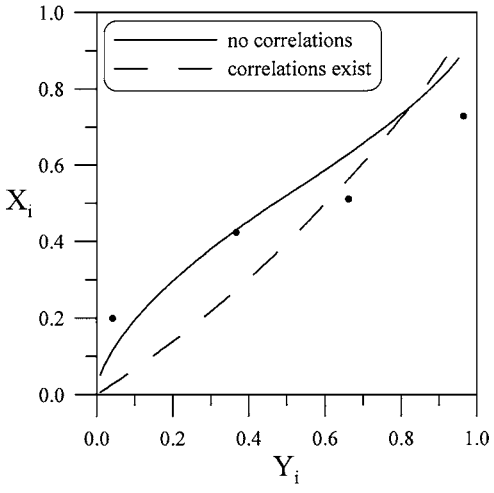


Figure 7. Single and mixed-gas adsorption of C_3H_8 and CO_2 on the H-mordenite (Talu and Zwiebel, 1986) at the temperature $T = 303.15$ K and the constant total pressure $P = 40.93$ kPa. Comparison with the experiment (●, ○) of the X-Y composition diagrams calculated by applying Eq. (27) (solid line, $Error = 1.07 \times 10^{-2}$) and Eq. (28) (dashed line, $Error = 2.23 \times 10^{-2}$). The theoretical phase diagrams were calculated with the assumption $W_{ij} = 0$.

Conclusion

Our theoretical study presents relatively simple equations for predicting mixed-gas phase diagrams. The model of calculations is based on the Integral Equation (IE) Approach and non-symmetrical energy distribution function (7). In effect, we present two different equations describing mixed-gas adsorption equilibria for the case of high correlations (28) and lack of correlations between energies of adsorbed molecules (27).

Our Eqs. (22), (27) and (28) were examined using a few adsorption systems (Van der Vaart et al., 2000; Szepesy and Illes, 1963; Dreisbach et al., 1999). Excellent agreement between the single-gas adsorption isotherms and the DA equation (22) is found. In the case of phase diagrams, except for the adsorption data published by Van der Vaart et al. (2000), we obtain poor agreement with the experimental data. But it can be stated that the adjustment of DA equation (22) to the experimental single-gas adsorption data reflects the correlation effects between the energies of adsorbed molecules. Namely, if the heteriogeneity parameters r and E determined from DA adjustment (22) to the single adsorption isotherms are different, the model assuming lack of correlations between the energies of adsorbed molecules (27) is more effective (see Fig. 2). If the values of r and E for mixture components are similar, we observe better agreement of the model assuming high correlations (28) with the experimental data.

It is necessary to note that our theoretical phase diagrams can reflect the existence of azeotropic behaviour in mixed-gas adsorption.

Nomenclature

Latin Symbols

N_t	Adsorbed amount (mol/kg)
M	Total number of sites, expressed in the same units as N_t
p	Partial pressure (MPa)
r	Heterogeneity parameter apperared in Eq. (7)
E	Heterogeneity parameter apperared in Eq. (7)
T	Temperature (K)
k	Boltzmann constant (J/K)
K	Langmuir constant (1/MPa)
p^l	Parameter appearing in Eq. (11) (MPa)
W	Interchange energy defined in Eq. (24) (J)
X	Mole fraction in the adsorbed phase
Y	Mole fraction in the gas phase

Greek Symbols

θ_t	Average fraction of surface coverage
$\chi(\varepsilon)$	Adsorption energy distribution function (1/J)
θ	Local fractional coverage
Ω_n	n-Dimensional physical domain of adsorption energies
ε	Adsorption energy (J)
ε^m	The maximum value of adsorption energy (J)
ε^l	The minimum value of adsorption energy (J)
ε^0	The most probable value of adsorption energy (J)
ε^c	Condensation energy (J)
$\aleph(\varepsilon)$	Integral form of $\chi(\varepsilon)$
ω	Interaction energy parameter between molecules adsorbed on neighbouring sites (J)

Subscripts

i	Component number

Acknowledgment

The author expresses his gratitude to Dr. Jolanta Narkiewicz-Michalek for valuable discussions.

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