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PREDICTION OF MULTI-SOLUTE ADSORPTION BY MEANS OF THE PARAMETERS CHARACTERIZING SINGLE-SOLUTE ADSORPTION SYSTEMS

Dubinin-Radushkevich (DR) and Freundlich equations derived on the basis of the general theory of multicomponent adsorption on energetically heterogeneous solid surfaces are used to describe the single-solute and bi-solute adsorption from dilute aqueous solutions on activated carbons. Both equations show a good linearity for single-solute and bi-solute experimental data. Moreover, the adsorption parameters of DR and Freundlich equations show a good correlation for single-solute and bi-solute data. This fact enables the prediction of multi-solute adsorption by means of the single-solute adsorption parameters.

1. INTRODUCTION

Adsorption of organic compounds from dilute aqueous solutions by activated carbons is a very important process in many fields of science and technology. Considering the fact that the measurements of multi-solute adsorption are much labor-consuming, the prediction of the latter by means of single-solute adsorption data is of a particular significance in practice. Thus, theoretical results in this field may be useful to programming a great number of technological processes, such as wastewater treatment or recovery of chemical compounds from industrial wastewaters.

While describing theoretically adsorption equilibria in multi-solute systems, it is possible to employ recent achievements concerning the adsorption from multicomponent gas and liquid mixtures on energetically heterogeneous solid surfaces [5—7]. Based on this theory many multicomponent isotherms describing the adsorption from dilute solutions were derived for different energy distributions [1]. Two of them, i.e. Dubinin-Radushkevich (DR) and Freundlich isotherms, were used in their traditional forms to describe single-solute adsorption data only [3, 13]. These forms, generalized to multi-solute adsorption, may be used to characterize adsorption equilibria in multicomponent systems [2, 8, 9, 12].

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In this paper, the generalized forms of DR and Freundlich-type isotherms have been used to describe single-solute and bi-solute adsorption data. The parameters of both equations obtained for single-solute adsorption have been compared with the bi-solute ones. DR and Freundlich isotherms have been, moreover, compared considering their usefulness for description of the adsorption in dilute solutions.

2. THEORETICAL

Basing on the general formulation of mixed-gas adsorption on heterogeneous solid surfaces, DR and Freundlich-type isotherms have been derived for multi-solute adsorption from dilute solutions [1, 8, 9]. The both isotherms are special forms of a more general "exponential" equation which is well known in the theory of gas adsorption [10]:

$$Q_{(n)} = \exp\left[\sum_{j=1}^{J} B_{1j}\left(RT\ln\frac{z_{(n)}}{A_1^0}\right)^j\right],\tag{1}$$

where B_{1j} (for $j = 1, 2, ..., J$) are heterogeneity parameters characterizing the shape of the distribution function, A_1^0 is a constant connected with the minimum value of E_i (the difference of adsorption energies for the i-th solute and solvent) and determines the position of the distribution on the energy axis. The variables $z_{(n)}$ and $Q_{(n)}$ are defined as follows:

$$z_{(n)} = c_1 + \sum_{i=1}^{n} K_{i1} c_i,\tag{2}$$

$$Q_{(n)} = \sum_{i=1}^{n} Q_{i(n)}.\tag{3}$$

In the above $Q_{i(n)}$ is the relative adsorption of the i-th solute, c_i is the concentration of the i-th solute in the bulk solution, and

$$K_{i1} = K_i/K_1 = a_i/a_1 \exp\left(\frac{E_i - E_1}{RT}\right),\tag{4}$$

K_i being the Langmuir's constant for the i-th solute and a_i — the pre-exponential factor. The partial isotherm $Q_{i(n)}$ is expressed as follows:

$$Q_{i(n)} = \frac{K_{i1} c_i}{z_{i(n)}} Q_{(n)} \quad \text{for } i = 1, 2, ..., n.\tag{5}$$

The "exponential" equation (1) has been derived by assuming that the heterogeneity parameters B_{1j} (for $j = 1, 2, ..., J$) are identical for all solutes and the difference of adsorption energies $(E_i - E_1)$ is independent of the type of adsorption sites. It means that

the distribution functions of adsorption energies have identical shape for all single-solute systems being only shifted on the energy axis.

For a specific class of the parameter B_{1j} the following expressions for DR and Freundlich-type isotherms may be derived:

$$Q_{(n)} = \left(\frac{z_{(n)}}{A_1^0}\right)^{B_{11}RT}; \quad B_{11} > 0 \quad \text{and} \quad B_{1j} = 0 \quad \text{for } j = 2, 3, \ldots, J, \tag{6}$$

$$Q_{(n)} = \exp\left[B_{12}\left(RT\ln\frac{z_{(n)}}{A_1^0}\right)^2\right]; \quad B_{12} < 0 \quad \text{and} \quad B_{1j} = 0 \quad \text{for } j = 1, 3, \ldots, J. \tag{7}$$

Eq. (6), i.e. Freundlich-type isotherm, corresponds to the exponential distribution function of adsorption energies, whereas eq. (7), DR-type isotherm, corresponds to the quasi-gaussian one.

For bi-solute adsorption eqs. (6) and (7) give:

$$Q_{12} = A_1(c_1 + K_{21}c_2)^m, \tag{8}$$

where

$$m = B_{11}RT \quad \text{and} \quad A_1 = (A_1^0)^{-m}$$

and

$$Q_{12} = \exp\left[-B_1\left(RT\ln\frac{c_1 + K_{21}c_2}{A_1^0}\right)^2\right], \tag{9}$$

where $B_1 = -B_{12}$.

However, for single-solute adsorption we obtain:

$$Q_i = A_i(c_i)^{-m}{}_i, \tag{10}$$

$$Q_i = \exp\left[-B_i\left(RT\ln\frac{c_i}{A_i^0}\right)^2\right]. \tag{11}$$

The eqs. (8)—(11) will be used to determine the adsorption parameters A_1, m, B_1, A_1^0 and A_i, m_i, B_i, A_i^0 from the bi-solute and single-solute experimental data.

3. RESULTS AND DISCUSSION

To check the eqs. (8)—(11) the experimental data obtained for single-solute and bi-solute adsorption from dilute aqueous solutions on activated carbon at 293 K [4] have been used. In this paper the results of theoretical considerations are presented for two single-solute systems: p-nitrophenol and p-chlorophenol and for one bi-solute system: p-nitrophenol + p-chlorophenol. The parameters for single-solute adsorption were evaluated from the following linear forms of Freundlich and DR-type equations:

$$\ln N_i = \ln A_i + m_i \ln c_i, \quad Q_i = N_i/N_m \tag{12}$$

and

$$(-\ln Q_i)^{1/2} = \sqrt{B_i}\,RT\ln A_i^0 - \sqrt{B_i}\,RT\ln c_i, \tag{13}$$

where N_i is the adsorbed amount of the i-th solute, and N_m is the maximum amount adsorbed in the monolayer.

In order to obtain the parameters for bi-solute adsorption the following forms of Freundlich and DR isotherms were used:

$$\ln(N_1 + N_2) = \ln A_1 + m\ln(c_1 + K_{21}c_2) \tag{14}$$

and

$$(-\ln Q_{12})^{1/2} = \sqrt{B_1}\,RT\ln A_1^0 - \sqrt{B_1}\,RT\ln(c_1 + K_{21}c_2). \tag{15}$$

As it has been mentioned in theoretical considerations, Freundlich-type equation corresponds to the exponential energy distribution, while DR-type isotherm relates to quasi-gaussian one. Many experimental and theoretical studies give the evidence that quasi-gaussian distribution function is characteristic of the numerous types of activated carbon and the isotherms corresponding to this type of distribution are more adequate for the description of the adsorption from dilute solutions on carbons than the equations related to exponential functions [1, 8, 11]. However, for many experimental systems, characterized by quasi-gaussian distribution functions, the exponential region is observed in a certain interval of adsorption energies. Thus, such systems may be described by quasi-gaussian isotherms within the whole region of adsorption energies, and within a narrow interval of energies — represented also by exponential isotherms.

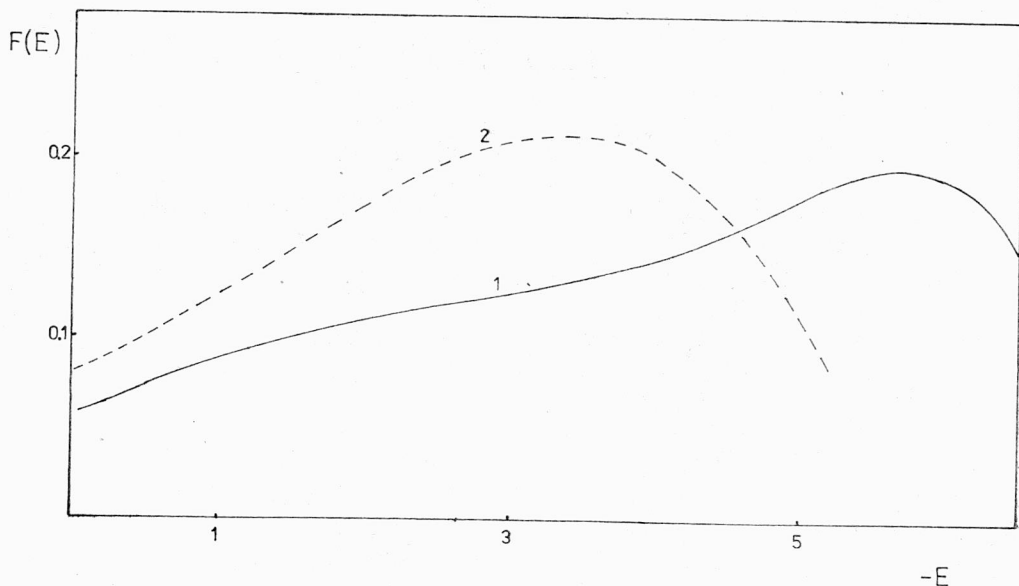Fig. 1 shows the distribution functions of adsorption energies for two single-solute

Fig. 1. Distribution functions of adsorption energies for adsorption of p-nitrophenol (1) and p-chlorophe nol (2) from dilute aqueous solutions on activated carbon at 293 K

Rys. 1. Dystrybuanta energii adsorpcji dla adsorpcji p-nitrofenolu (1) i p-chlorofenolu (2) na węglu aktywnym w 293 K z rozcieńczonych roztworów wodnych

systems investigated: p-nitrophenol and p-chlorophenol. These functions have been evaluated by using the method analogical to that described by JARONIEC [10]. For both the systems the distribution functions have in general quasi-gaussian shape, but Freundlich's region is observed in a certain interval of adsorption energies. Thus, both the isotherms may be used to describe adsorption of the two systems investigated. Figs. 2a and 3a represent the linear Freundlich (12) and DR (13) dependences for adsorption of p-
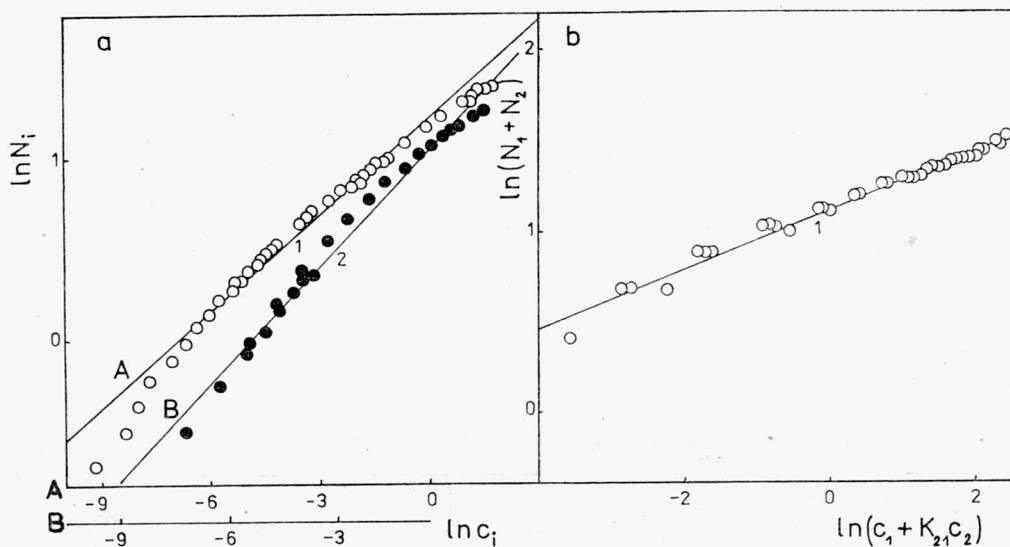

Fig. 2. Linear Freundlich equations (12) and (14) for adsorption of: a) single-solute systems (p-nitrophenol (*1*) and p-chlorophenol (*2*)); b) bi-solute system (p-nitrophenol + p-chlorophenol) from dilute aqueous solutions on activated carbon at 293 K

Rys. 2. Liniowe równania Freundlicha (12) i (14) dla adsorpcji: a) układów pojedynczych substancji rozpuszczonych (p-nitrofenol (*1*) i p-chlorcfenol (*2*)), b) układu dwóch substancji rozpuszczonych (p-nitrofenol + p-chlorofenol) na węglu aktywnym w 293 K z rozcieńczonych roztworów wodnych

nitrophenol and p-chlorophenol from dilute aqueous solutions on activated carbon; the DR isotherm shows very good linearity for both single-solute systems, whereas Freundlich equation shows some deviations from linearity at low and high concentrations. These results correspond very well with the shape of distribution functions presented in fig. 1. The parameters A_i, m_i and A^0, B_i, evaluated according to eqs. (12) and (13) for single-solute systems, are summarized in tab. 1. The heterogeneity parameters m_i and B_i for p-nitrophenol and p-chlorophenol being similar, the assumption of equality of m_i- and B_i-values for solutes forming bi-solute mixture is fulfilled. Figs. 2b and 3b present the linear dependences (14) and (15) for the mixture: p-nitrophenol + p-chlorophenol. For this bi-solute system both the isotherms show good linearity without any deviations. The parameters: A_1, m, K_{21} and A_1^0, B_1, K_{21}, N_m of these equations are summarized in tab. 2. By comparing the values presented in tabs. 1 and 2 we can see that the parameters for single-solute and bi-solute adsorption show a good correlation. This fact enables

the prediction of bi-solute adsorption by using the parameters obtained for single-solute adsorption.

Finally, the following conclusions can be formulated:

DR equation gives a good representation of the bi-solute and single-solute systems within the whole range of concentrations, whereas Freundlich equation shows some deviations at low and high values of concentrations.
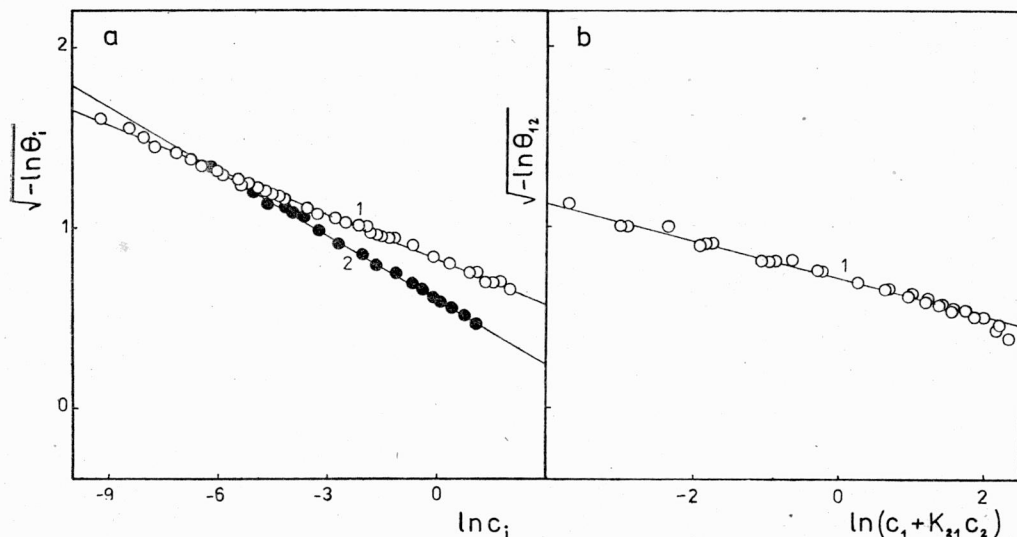
Fig. 3. Linear DR equations (13) and (15) for adsorption of: a) single-solute systems (p-nitrophenol (*1*) and p-chlorophenol (*2*)), b) bi-solute system (p-nitrophenol + p-chlorophenol) from dilute aqueous solutions on activated carbon at 293 K

Rys. Liniowe równania Dubinina-Radushkevicha (13) i (15) dla adsorpcji: a) układów pojedynczych substancji rozpuszczonych (p-nitrofenol (*1*) i p-chlorofenol (*2*)), b) układu dwóch substancji rozpuszczonych (p-nitrofenol + p-chlorofenol) na węglu aktywnym w 293 K z rozcieńczonych roztworów wodnych

Table 1

Parameters A_i, m_i and A_i^0, B_i, evaluated according to the Freundlich (12) and DR (13) equations, characterizing the adsorption of p-nitrophenol and p-chlorophenol from dilute aqueous solutions on activated carbon at 293 K

Parametry A_i, m_i i A_i^0, B_i, obliczone na podstawie równania Freunlicha (12) i Dubinina-Radushkevicha, charakteryzujące adsorpcję p-nitrofenolu i p-chlorofenolu na węglu aktywnym w 293 K z rozcieńczonych roztworów wodnych

Solute	Freundlich equation		DR equation		
	A_i	m_i	N_m [mmol/g]	$\ln A_i^0$ —	$B_i \times 10^9$ [mol/J]^2
p-nitrophenol	3.4	0.18	6.5	10.1	1.1
p-chlorophenol	3.2	0.21	4.4	5.0	2.4

Table 2

Parameters A_1, m and A_1^0, B_1, evaluated according to the Freundlich (14) and DR (15) equations, characterizing the adsorption of p-nitrophenol + p-chlorophenol mixture from dilute aqueous solutions on activated carbon at 293 K

Parametry A_1, m i A_1^0, B_1, obliczone na podstawie równania Freundlicha (14) i Dubinina-Radushkevicha (15), charakteryzujące adsorpcję mieszaniny p-nitrofenolu z p-chlorofenolem na węglu aktywnym w 293 K z rozcieńczonych roztworów wodnych

System	Freundlich equation				DR equation		
	K_{21}	A_1	m	N_m [mmol/g]	K_{21}	$\ln A_1^0$	$B_1 \times 10^9$ [mol/J]^2
p-nitrophenol + p-chlorophenol	1.2	3.0	0.17	5.4	1.0	6.8	1.9

Good correlation being observed between adsorption parameters of both equations for single-solute and bi-solute adsorption proves that the prediction of bi-solute adsorption by means of the parameters for single-solute adsorption is possible.

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PRZEWIDYWANIE ADSORPCJI WIELU ROZPUSZCZONYCH SUBSTANCJI ZA POMOCĄ PARAMETRÓW CHARAKTERYSTYCZNYCH DLA ADSORPCJI UKŁADÓW Z JEDNĄ SUBSTANCJĄ ROZPUSZCZONĄ

Zastosowano równania Dubinina-Radushevicha (DR) i Freundlicha, wyprowadzone na podstawie ogólnej teorii wieloskładnikowej adsorpcji na energetycznie heterogenicznych powierzchniach ciał stałych, do opisu adsorpcji na węglu aktywnym rozpuszczonych substancji pojedynczych i dwuskładnikowych

pochodzących z rozcieńczonych roztworów wodnych. Stwierdzono liniowość obu równań dla danych eksperymentalnych dotyczących pojedynczych i dwuskładnikowych substancji rozpuszczonych. Stwierdzono ponadto, że parametry adsorpcji równań DR i Freundlicha dobrze korelują z danymi eksperymentalnymi dla pojedynczych i dwuskładnikowych substancji rozpuszczonych. Fakt ten pozwala przewidywać adsorpcję wielu substancji rozpuszczonych na podstawie parametrów adsorpcji pojedynczych substancji rozpuszczonych.

VORAUSSICHT DER ADSORPTION ZAHLREICHER GELÖSTEN SUBSTANZEN MIT HILFE FÜR DIE ADSORPTION EINER SUBSTANZ FESTGELEGTEN PARAMETER

Zur Anwendung kamen die Formeln von Dubinin-Radushevich (DR) und Freundlich — abgeleitet von der allgemeinen Theorie der Mehrstoffadsorption auf energetisch heterogenen Feststoffoberflächen; sie dienten zur Beschreibung der Adsorption von gelösten, einzelnen und binären Substanzen, die aus verdünnten Wasserlösungen stammten, auf Aktivkohlen. Festgestellt wurden lineare Beziehungen beider Formeln für einzelne und binäre Substanzen. Weiterhin konnte man feststellen, daß die Adsorptionsparameter nach DR und Freundlich gut mit den Versuchsergebnissen übereinstimmen. Aufgrund der hier wiedergegebenen Erörterungen, kann man den Verlauf der Mehrstoffadsorption voraussehen.

ПРЕДВИДЕНИЕ АДСОРБЦИИ МНОГИХ РАСТВОРЁННЫХ ВЕЩЕСТВ С ПОМОЩЬЮ ПАРАМЕТРОВ, ХАРАКТЕРНЫХ ДЛЯ АДСОРБЦИИ СИСТЕМ С ОДНИМ РАСТВОРЁННЫМ ВЕЩЕСТВОМ

Применены уравнения Дубинина-Радушевича (ДР) и Фройндлиха, выведенные на основе общей теории многокомпонентной адсорбции на энергетически гетерогенных поверхностях твёрдых тел, для описания адсорбции на активированном угле растворённых одиночных и двухкомпонентных растворённых веществ, происходящих из разбавленных водных растворов. Была выявлена линейность обоих уравнений для экспериментальных данных, касающихся одиночных и двухкомпонентных растворённых веществ. Кроме того, было отмечено, что параметры адсорбции уравнений ДР и Фройндлиха хорошо коррелируют с экспериментальными данными для одиночных и двухкомпонентных растворённых веществ. Этот факт позволяет предвидеть адсорбцию многих растворённых веществ на основе параметров адсорбции одиночных растворённых веществ.