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Global Non-Ideality Effects in Adsorption of Organic Substances from Dilute Aqueous Solutions on Activated Carbon

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Summary. A method for the quantitative estimation of the global non-ideality of the adsorption of weak organic electrolytes on activated carbon from dilute aqueous solutions is presented. The method is based on the analysis of a *Graham* plot which reflects the adsorption isotherm deviations from ideality. Averaging these deviations over the whole range of adsorption, one gets a single value representing the global non-ideality of a system. The method also allows to estimate the contributions of heterogeneity and interactions in the adsorbed phase to the global non-ideality effect. The theoretical considerations are illustrated by some model calculations. The usefulness of the method is tested for experimental data of benzoic and salicyclic acid adsorption over a wide range of *pH* and concentrations.

Keywords. Dilute aqueous solutions; Adsorption of organic solutes; Non-ideality effects in adsorption.

Globaler Effekt der Nicht-Idealität bei der Adsorption organischer Substanzen aus verdünnten wässerigen Lösungen an Aktivkohle

Zusammenfassung. Es wird eine Methode zur quantitativen Abschätzung der globalen Nicht-Idealität für die Adsorption schwacher organischer Elektrolyte aus verdünnten wässerigen Lösungen an Aktivkohle vorgestellt. Diese Methode basiert auf der Analyse der bekannten *Graham*-Abhängigkeit, die die Abweichung der Adsorptionsisotherme von der Idealität zeigt. Bei Errechnung des Durchschnittwertes dieser Abweichung über den ganzen Asorptionsbereich erhält man einen Wert, der die globale Nicht-Idealität für ein Adsorptionssystem charakterisiert. Die Methode erlaubt auch, den Beitrag der Heterogenität und der Wechselwirkungen in der Adsorptionsphase zum globalen Effekt der Nicht-Idealität abzuschätzen. Die theoretischen Erörterungen werden an Hand von Modellberechnungen illustriert. Die Nutzbarkeit der Methode wurde mit experimentellen Daten der Benzoe- und Salicylsäureadsorption in einem weiten Bereich von *pH* und Konzentration getestet.

Introduction

Most experimental adsorption systems show significant deviations from ideal behaviour caused by the energetic heterogeneity of the adsorbent, lateral interactions of adsorbed molecules in surface or bulk phases, or–in the case of ion adsorption – by electrostatic interactions. Thus, these effects should be taken into account in the theoretical description of the adsorption process. From the practical point of view it is very important to estimate quantitatively the influence of these effects on the adsorption equilibrium. In the literature, several methods were proposed [1–4] for the description and evaluation of the energetic heterogeneity and interaction effects.

Studies concerning the influence of energetic heterogeneity and lateral interactions on adsorption have shown that the two effects compensate each other to a certain degree [5]. In some specific well-defined systems with known physical properties and very precisely measured experimental isotherms, it was possible to separate and evaluate the heterogeneity and lateral interaction effects [6]. However, for most systems, measuring the experimental isotherms and estimating the non-ideality effects by optimizing the parameters of theoretical isotherms, one can obtain the compensated values reflecting the total deviations from ideality. Thus, it seems to be reasonable to calculate the global non-ideality effect observed in the course of experimental isotherm.

In this paper, a method is proposed to evaluate quantitatively the global deviation from ideality for the adsorption from dilute aqueous solutions of organic substances on activated carbon. The method is based on the theory of physical adsorption of gases and liquids on solid surfaces. The effects of energetic heterogeneity of adsorbent, specific and non-specific interactions in the adsorbed phase, and electrostatic interactions between adsorbed molecules and charged solid surfaces, are taken into account. The theoretical considerations are illustrated by model calculations and tested against experimental data for benzoic and salicylic acid adsorption on activated carbon.

Results and Discussion

Graham [7] proposed a useful method to study deviations from ideality in gas adsorption systems, based on the dependence of the quantity $[\theta_t/(1-\theta_t)]$ on the gas pressure p. It allows to classify experimental systems with regard to the sources of these deviations: lateral interactions in the adsorbed phase or surface heterogeneity. This idea was then modified [6] by introducing a new function characterizing the general system heterogeneity. For the adsorption from dilute aqueous solutions of an organic substance on a solid, we may define a function h

$$h = \frac{\partial \ln c}{\partial \ln [\theta_t/(1-\theta_t)]} \tag{1}$$

where c is the solute concentration and θ_t is the total relative adsorption.

Averaging h over the whole range of adsorption one obtains

$$H = \int_{\theta_t=0}^{1} \frac{\partial \ln c}{\partial \ln [\theta_t/(1-\theta_t)]} \mathrm{d}\theta_t = \int_{c(\theta_t=0)}^{c(\theta_t=1)} \theta_t(1-\theta_t)\mathrm{d}\ln c \tag{2}$$

The function $h(\theta_t)$ and its integral, H, may be used as a measure of the deviation from ideality for a given adsorption system. In the case of the *Langmuir* isotherm describing the ideal adsorption on a homogeneous solid without any interactions among adsorbed molecules, $h(\theta_t)$ is constant and equal to unity and thus $H = 1$, too. With increasing heterogeneity of the system, an increase of both function values is observed. The opposite tendency was found for systems showing attractive lateral interactions in the absorbed phase; any increase of their contribution to the total nonideality effect results in a decrease of both function values. The detailed discussion of H and h function properties for gas adsorption was presented elsewhere [6].

Let us discuss the H and h function behavior for some model isotherms based on the physical adsorption theory of heterogeneous solids. Generally, the isotherm equation may be written as follows:

$$\theta_t = \int_{\Delta E} \theta_1 \chi(E) \mathrm{d}E = \int_{\Delta E} \frac{g(c,E)}{1+g(c,E)} \chi(E) \mathrm{d}E \qquad 3$$

Here, θ_1 is the local adsorption on a surface patch of constant energy, $g(c, E)$ is the function depending on the adsorption model assumed, $\chi(E)$ is the distribution function of reduced adsorption energies $E(E = \varepsilon/\mathrm{R}T$, ε: adsorption energy), ΔE is the integration range, R is the gas constant, and T is the temperature.

When the function $g(c, E)$ depends linearly on the concentration (*e.g.* for the Langmuir local isotherm)

$$c\frac{\mathrm{d}g(c,E)}{\mathrm{d}c} = g(c,E) \qquad 4$$

it is possible to clarify the meaning of $h(\theta_t)$ and its relation to H:

$$H = \int_0^1 \frac{\int_{\Delta E} \theta_1 \chi(E)\mathrm{d}E \left[1 - \int_{\Delta E} \theta_1 \chi(E) \mathrm{d}E\right]}{\int_{\Delta E} \theta_1 (1-\theta_1)\chi(E)\mathrm{d}E} \mathrm{d}\theta_t = \int_0^1 \frac{\theta_t(1-\theta_t)}{\int_{\Delta E} \theta_1(1-\theta_1)\chi(E)\mathrm{d}E} \mathrm{d}\theta_t \qquad 5$$

According to the assumed model of the adsorption process, g may be written as follows:

–for non-dissociated species:

$$g(c,E) = g(c,E,pH) = Kc \qquad 6$$

where K is the equilibrium constant connected with adsorption energy:

$$K = K_0 \exp(E) \qquad 7$$

–for ionic species [8]:

$$g(c,E,pH) = Kcg_q \qquad 8$$

where

$$g_q = \exp(-z_{\pm}\mathrm{F}\phi_s/\mathrm{R}T) \qquad 9$$

$z_{\pm}$ is the charge of the organic ion, F is the Faraday constant, and ϕ_s is the electric interfacial potential being a function of surface charge density q_s, and solution ionic strength I. The surface charge q_s is balanced by the charge density due to adsorbed ions and by the charge density of diffuse double layer.

–for the species interacting in absorbed phase:

$$g(c,E) = Kcg_{\mathrm{int}}(\theta) \quad \text{where} \quad \theta = \theta_t \text{ or } \theta_1 \qquad 10$$

For a random topography of adsorption sites, the function g depends on the total coverage θ_t; for a patchwise topography it depends on the local coverage θ_l.

In Fig. 1 the dependences of H *vs.* energy dispersion σ are presented for the *Langmuir* local isotherm (Eq. 6) and two distribution functions of adsorption energies: *Gauss* (G) and quasigaussian *Langmuir-Freundlich* (LF) [9]. The gaussian distributions well characterize the energetic heterogeneity of the adsorption from dilute solutions of organic solutes on activated carbon [10]. The *Gauss* function well describes the real adsorption systems; it gives the *Henry* range, but does not correspond to an analytical adsorption isotherm. On the other hand, the quasigaussian LF distribution well characterizes the real adsorption systems over a range of intermediate coverages, but does not give the *Henry* range; however, it corresponds to a simple analytical isotherm, and thus is very useful from a practical point of view. Fig. 1A shows the dependence of H on σ for a *Gauss* distribution.

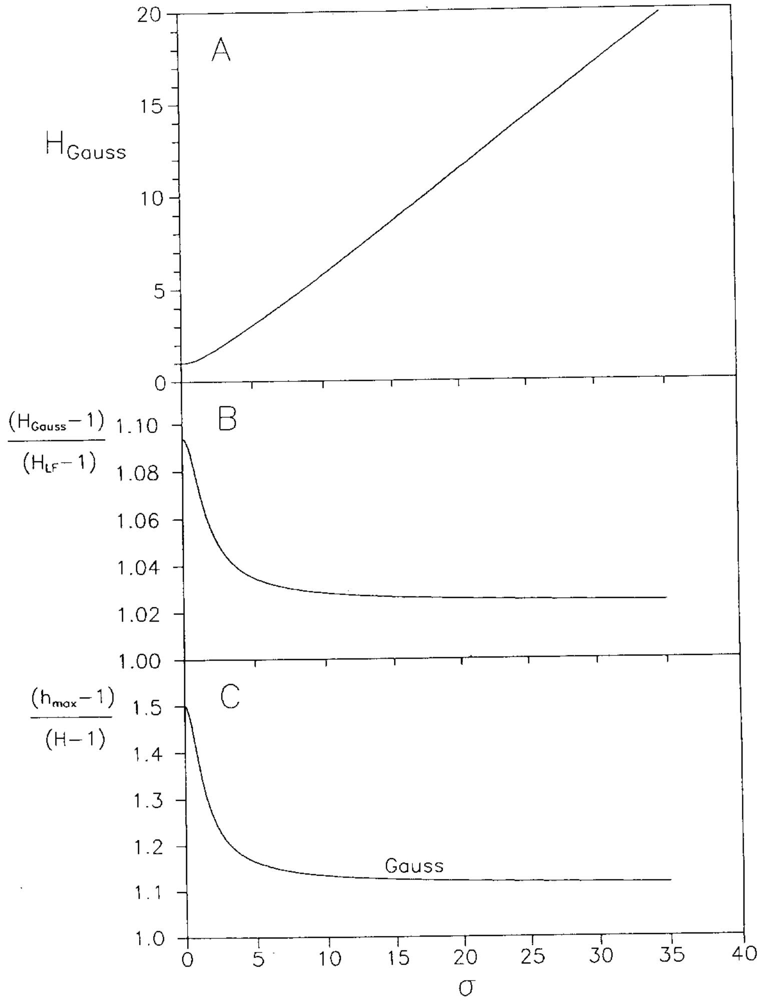

Fig. 1. A: plot of the function H *vs.* energy dispersion σ for the isotherm corresponding to a *Gauss* energy distribution function; B: comparison of H *vs.* σ for the *Langmuir-Freundlich* isotherm and for the isotherm corresponding to the *Gauss* distribution; C: function $(h_{max} - 1)/(H - 1)$ *vs.* σ for the *Gauss* isotherm

With an increase of the energetic heterogeneity σ, an increase of H is observed. For small σ values only a weak deviation ($[H-1] \sim \sigma^2$) from *Langmuir* behavior ($H = 1$) can be noticed. However, for higher σ values the dependence $H = \mathrm{f}(\sigma)$ becomes linear. In Fig. 1B, the course of H is compared for the *Gauss* and *Langmuir-Freundlich* ($H_{\mathrm{LF}}(\sigma) = [1 + 3(\sigma/\pi)^2]^{1/2}$) distributions. Fig. 1C presents the dependence $(h_{\max} - 1)/(H-1)$ which characterizes an approximate shape of function $h(\theta_t)$, determining a deviation of $h_{\max}$ from an average value for different values of energy dispersion σ. It allows to estimate in a simple way a deviation of $H_{\exp}$ calculated for a limited range of surface coverages $\langle \theta_{t1}, \theta_{t2} \rangle$ (as a rule over a range of average coverages $h(\theta_t) > H$) from the theoretical value H_{theor}.

Figure 2 presents the dependences of h on θ_t for the *Langmuir* and *Langmuir-Freundlich* isotherms, and for the isotherm corresponding to a *Gauss* distribution for three values of energy dispersion: $\sigma = 0.001$ (A), 4.75 (B), and 35 (C). These σ values were chosen in order to study a possibly wide range of energetic heterogeneity. However, for the activated carbons the typical values of σ are contained over the range 5–10. The value $\sigma = 4.75$ corresponds to the experimental system: aqueous solution of benzoic acid – RIC activated carbon [5]. A distinct change of $h(\theta_t)$ dependence type is observed for small σ value (extremely low heterogeneity) (Fig. 1A) in comparison to high σ values (high and extremely high heterogeneity) (Figs.

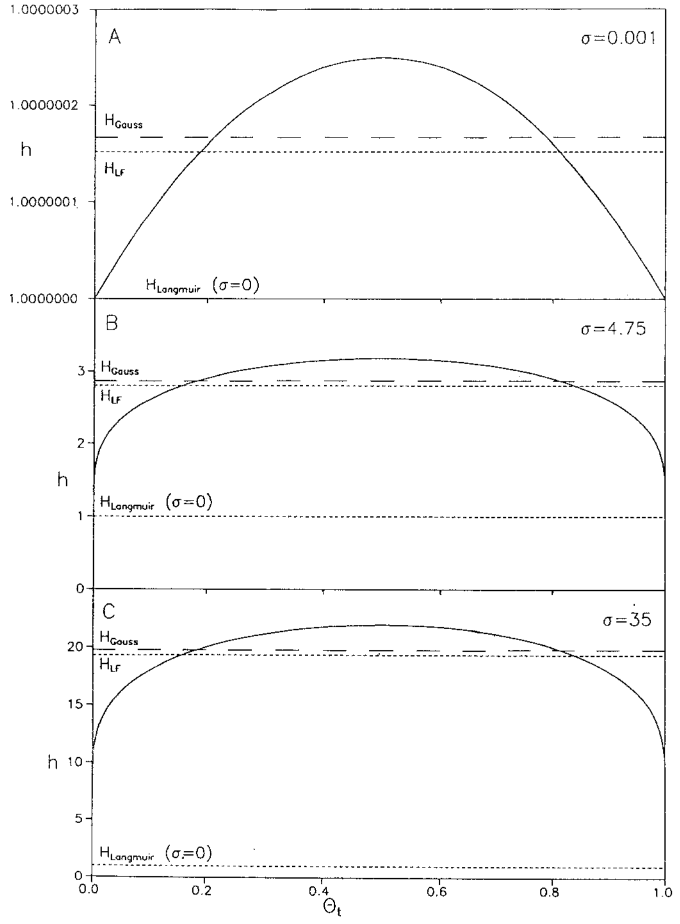

Fig. 2. Plot of the function h *vs.* surface coverage θ_t for different values of energy dispersion: σ = 0.001 (A), 4.75 (B), 35 (C), and for the isotherms corresponding to *Gauss* and *Langmuir-Freundlich* (LF) distributions

1B, C). Additionally, with increasing σ, the similarity of the function h for the *Gauss* and LF distributions increases.

The comparison of the curves presented in Figs. 1 and 2 indicates that the isotherms corresponding to Gauss and LF distributions show similar behavior. In Fig. 3, the *Langmuir* isotherm (Eq. 6) and the *Langmuir-Freundlich* isotherm

$$\theta_t = \frac{(\bar{K}c)^m}{1+(\bar{K}c)^m}, \quad \bar{K} = K_0 \exp(\bar{E}/RT), \quad H = (1/m) \tag{11}$$

($\bar{E}$ is the mean adsorption energy, m the heterogeneity parameter), and the isotherm corresponding to a *Gauss* distribution are drawn in the coordinates $\ln[\theta_t/(1-\theta_t)]$ *vs.* $\ln(\bar{K}c)$ for two values of energy dispersion: $\sigma = 4.75$, 35. In these coordinates, the *Langmuir* and *Langmuir-Freudlich* equations show linear behavior. The *Gauss* isotherm becomes very similar to the LF equation in a range of intermediate concentrations, but deviates from this linear relation at low and high concentrations. For this reason, the isotherms corresponding to G and LF distributions may both describe successfully the same experimental system over a range of intermediate concentrations. The LF isotherm has a simple analytical form, easy for use. However, its behavior is not correct for $\theta_t \to 0$ and $\theta_t \to 1$. For every isotherm showing correct physical properties for $\theta_t \to 0$ and $\theta_t \to 1$, the value of the function $h(\theta_t)$ should tend to unity. In practice, however, this inconsistency may not have significant importance.

In the case of dissociating organic substances, it is necessary to take into consideration the effect of electrostatic interactions between the adsorbed molecules and the charged surface. In Fig. 4, the results of studies on the effect of solution pH,

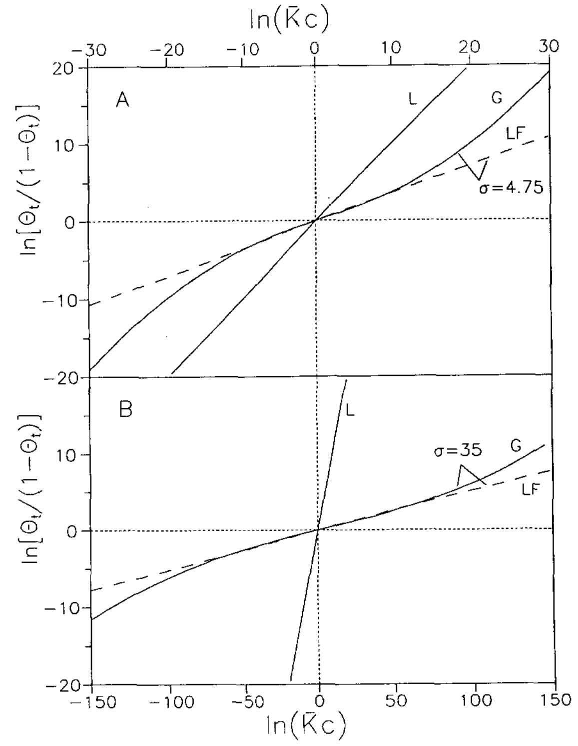

Fig. 3. Function $\ln[\theta_t/(1-\theta_t)]$ *vs.* $\ln(\bar{K}c)$ for the *Langmuir*, *Langmuir-Freundlich*, and *Gauss* isotherms and for two values of energy dispersion ($\sigma = 4.75$ (A), 35 (B))

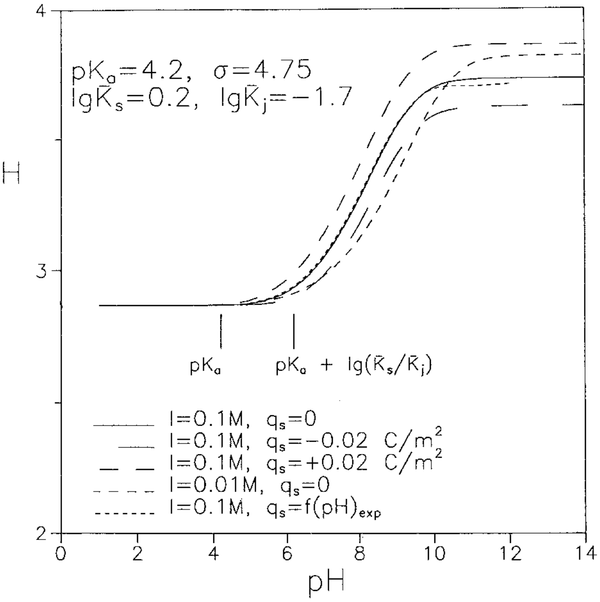

Fig. 4. Dependence of the function H on pH for the *Gauss* distribution of adsorption energies and for the local isotherm (Eqs. 6 and 7), taking into account the electrostatic interactions. The isotherm parameters are indicated in the figure. The calculations were performed for different values of solution ionic strength I, and surface charge density q_s. The experimental dependence $q_s = f(pH)$ is given in Fig. 5C

ionic strength, and surface charge density, on H are presented. The calculations were performed for the model *Gauss* isotherm corresponding to the experimental isotherm of benzoic acid adsorption from aqueous solution on RIC activated carbon [5] characterized by the optimized parameters indicated in the figure. The form of the g function may be written as follows:

$$g(c, E, pH) = K_s c_s + K_j c_j g_q \; (c = c_s + c_j,\ c_i = f_i(c, pH, pK_a),\ i = s, j) \qquad 12$$

Here, the subscripts (s) and (j) refer to the neutral and ionic forms of organic solute, and K_a is the dissociation constant.

The quantity H is a measure of differences among adsorption constants for adsorption on different sites. If an adsorbed substance (*e.g.* organic acid) is a mixture of ionized and neutral species (treated as one substance), the effective differentiation of adsorption constants increases significantly in comparison to a non-ionized absorbate. Thus, an increase of H is noticed. The greater the difference between adsorption constants for ionic and neutral species, the stronger is the increase of the function H. However, in the case of ion adsorption ($pH \gg pK_a$), an increase of H is also observed. It is caused by the changes of g_q with increasing concentration.

For low values of pH ($pH < pK_a$), no effect of pH, I and q_s on H is noticed; it is connected with energetic heterogeneity for neutral species only. For very high values of pH ($pH \gg pK_a$), a stabilization of the H function values is observed. For this pH range, the value of H depends on the changes of I and q_s. In the figure the values pK_a and $pK_a + \lg(\bar{K}_s/\bar{K}_j)$ are indicated. For $pH = pK_a$, the concentrations of both solute forms (ionic and neutral) are identical. However, for $pH = pK_a + \lg(\bar{K}_s/\bar{K}_j)$ the adsorption potentials connected with dispersive interactions become equal for both forms: $\bar{K}_s c_s = \bar{K}_j c_j$. A strong shift of the curves is relation to the point $pK_a + \lg(\bar{K}_s/\bar{K}_j)$ is a result of low values of factor g_q ($\ll 1$). It causes that the point $\bar{K}_s c_s = \bar{K}_j c_j g_q$ is reached for much higher pH values.

A decrease of ionic strength causes a decrease of H for the average pH values ($pH > pK_a$) and an increase for high pH values ($pH \gg pK_a$).

The effect of surface charge on H depends on the sign of the adsorbed ion. The same sign of surface charge and adsorbed ion causes a slight decrease of H in relation to the dependence $H = \mathrm{f}(pH)$ calculated for $q_s = 0$. The opposite tendency is observed when the surface charge and adsorbed ion have different signs. In the case of the curve obtained for the experimental dependence $q_s = \mathrm{f}(pH)$ [5], only a slight effect of q_s on H is observed.

Let us consider the possibility of a separation of a non-ideality effect from the total effect for the adsorption from a dilute aqueous solution of dissociating organic substance onto an activated carbon. In the description of adsorption equilibrium of this system the energetic heterogeneity of adsorbent as well as the electrostatic and lateral interactions in the adsorbed phase should be taken into account. Thus, the isotherm equation may be generally rewritten in the form [3]:

$$\theta_t = \theta_t(c') \qquad 13$$

where

$$c' = c g_q g_{\mathrm{int}} \qquad 14$$

Then, the H function may be transformed as follows:

$$H = \int \theta_t(1-\theta_t)\,\mathrm{d}\ln c = \int \theta_t(1-\theta_t)\,\mathrm{d}\ln c' - \int \theta_t(1-\theta_t)\,\mathrm{d}\ln g_q$$

$$- \int \theta_t(1-\theta_t)\,\mathrm{d}\ln g_{\mathrm{int}} = H_E - \Delta H_{\mathrm{el}} - H_{\mathrm{int}} \qquad 15$$

The observed (experimental) value of H describes the total non-ideality of a given adsorption system, which is a sum of the respective terms connected with the energetic heterogeneity H_E, lateral interactions of specific and non-specific character H_{int}, and electrostatic interactions ΔH_{el} (this term depends also on a general isotherm course – the effect can not be entirely separated). For some specific adsorption systems with well defined physical properties, one can calculate the values for H_{int}, H_E, and ΔH_{el}. The estimation of the ΔH_{el} term is possible from the adsorption data measured for non-dissociated species (*e.g.* for organic acids, when $pH < pK_a$); then, $\Delta H_{\mathrm{el}} = 0$ and $H = H_E - H_{\mathrm{int}}$. Moreover, measuring the adsorption isotherm for a homogeneous solid, one can estimate the term H_{int}; then, $H_E = 1$ and $H = 1 - H_{\mathrm{int}}$. However, for most experimental systems it is not possible to estimate the contributions of these terms to the total non-ideality effect.

The analysis of complex adsorption systems depends strongly on the chosen theoretical model. Taking into consideration several factors (*i.e.*, heterogeneity, electrostatic and lateral interactions) influencing the adsorption equilibrium one introduces many parameters to the model regarded. The increasing number of parameters characterizing an adsorption system increases the possibility of computational errors. Moreover, as it was stated in the analysis of experimental data [5], the effect of different factors, *e.g.* heterogeneity and lateral interactions, compensate mutually. The observed deviation from the ideal behavior is a sum of different effects. Thus, the H function may be very useful for a characterization of the global deviation from ideality of the system.

In order to study the usefulness of proposed procedure for estimating the global non-ideality of adsorption systems, experimental data for the adsorption of benzoic and salicylic acid from dilute aqueous solution on the activated carbon RIC at 293 K were chosen. These data were measured over a wide range of solution *pH* at a constant value of ionic strength $I = 0.1$ mol/l. Details of the experimental procedure are presented elsewhere [5]. In Fig. 5, the experimental points for the adsorption of benzoic and salicyclic acids are presented over a wide concentration range. The *H* function values were calculated directly from the experimental data by using the averaging ($\bar{H}_{exp}$) and trapezium approximation ($\bar{H}_{corr}$) methods. As was explained in the analysis of model calculations presented in Fig. 4, it is possible to estimate a part of the *H* function independently of electrostatic interactions from the experimental isotherms measured for $pH < pK_a$. The *H* value estimated in such a way corresponds to energetic heterogeneity and lateral interactions of dispersion force type. It may be used as a parameter characterizing mainly the energetic nonideality of the adsorption system (for the activated carbons the heterogeneity effects are predominant). Because of the limited range of experimentally measured surface coverages $\langle \theta_{t1}, \theta_{t2} \rangle$ for both systems studied, the approximate experimental *H* function values, $\bar{H}_{exp}$, were calculated directly from the experimental data by using the averaging procedure

$$\bar{H} = \frac{1}{\theta_{t2} - \theta_{t1}} \int_{c(\theta_{t1})}^{c(\theta_{t2})} \theta_t(1 - \theta_t)\mathrm{d}\ln c \tag{16}$$

The results of these calculations are presented in Table 1.

In order to estimate the correctness of *H* value evaluation for this limited range of experimentally measured surface coverages, these values were compared with the H_{corr} values obtained from another approximation procedure based on the general behaviour of $h(\theta_t)$, and with the H_{theor} values calculated for the parameters of theoretical isotherms (Table 1). The H_{corr} values were calculated using a trapezium

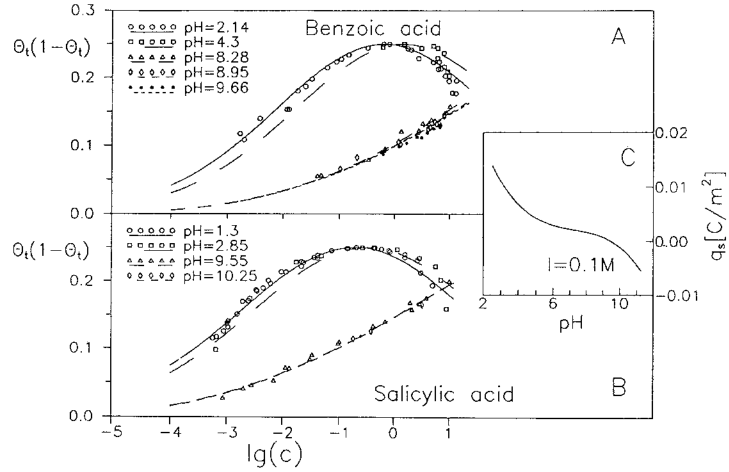

Fig. 5. Function $[\theta_t(1 - \theta_t)]$ *vs.* lg(*c*) calculated for the experimental data of adsorption from aqueous solutions of benzoic (A) and salicylic (B) acids on the activated carbon RIC at 293 K at different values of solution *pH* and at constant ionic strength $I = 0.1$ mol/l. The theoretical curves were drawn for the optimized parameters [5]. In Fig. 5C, the experimental dependence of surface charge density *vs.* *pH* determined from the potentiometric titration data is presented

Table 1. Comparison of H for two investigated adsorption systems: estimated from the experimental data by an averaging procedure ($\bar{H}_{\mathrm{exp}}$), evaluated using the approximation method (H_{corr}), and calculated for the optimized isotherm parameters [5] (H_{theor}); adsorption capacity: $a_{\mathrm{m}} = 4.7$ mmole/g

Adsorbate	$\bar{H}_{\mathrm{exp}}$	H_{corr}	H_{theor}	$\lg\bar{K}_{\mathrm{s}}$	$\lg\bar{K}_{\mathrm{j}}$	σ
Benzoic acid	3.08	2.65	2.87	0.196	−1.705	4.75
Salicylic acid	3.26	2.80	3.06	0.713	−0.828	5.12

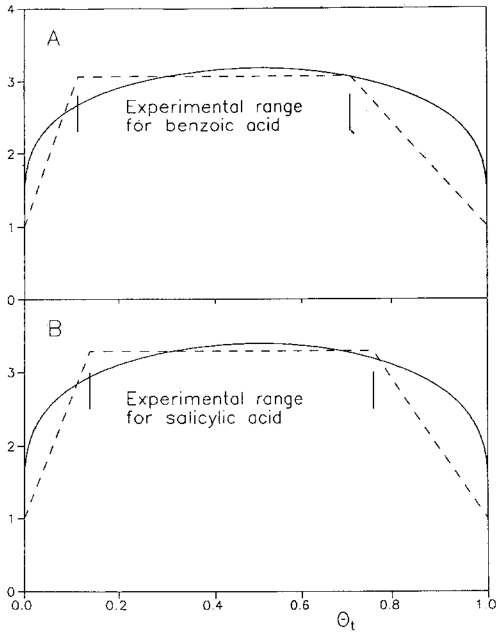

Fig. 6. Function h *vs.* θ_{t} calculated using a trapezium approximation procedure (dashed lines) and evaluated using the parameters of theoretical isotherms (Table 1) (solid lines) for the experimental systems aqueous solutions of benzoic (A) and salicyclic acids (B) – activated carbon RIC at 293 K [5]

approximation and assuming that $h = 1$ for $\theta_{\mathrm{t}} = 0$, $\theta_{\mathrm{t}} = 1$, and $h = \bar{H}$ for $\langle\theta_{\mathrm{t1}}, \theta_{\mathrm{t2}}\rangle$:

$$\bar{H}_{\mathrm{corr}} = \left(\frac{\bar{H}_{\mathrm{exp}} + 1}{2}\right)(\theta_{\mathrm{t1}} + 1 - \theta_{\mathrm{t2}}) + (\theta_{\mathrm{t2}} - \theta_{\mathrm{t1}})\bar{H}_{\mathrm{exp}} \qquad 17$$

However, the H_{theor} (*Gauss* energy distribution) values were calculated for $\theta_{\mathrm{t}} \in \langle 0, 1\rangle$. The results are presented in Fig. 6 and in Table 1.

The H function values estimated directly from the experimental data were then compared with the H_{theor} values calculated for the parameters of theoretical isotherm (Eq. 3) corresponding to the *Gauss* energy distribution function and for g functions expressed by Eq. 12. The isotherm parameters evaluated by the optimization procedure [5] are presented in Table 1. In Fig. 5, the experimental (points) and theoretical (lines – *Gauss* model for the parameters from Table 1) dependences $[\theta_{\mathrm{t}}(1-\theta_{\mathrm{t}})]$ *vs.* $\lg c$ are presented. A good agreement is observed between the experimental points and theoretical curves. The H_{theor} function values are presented in Table 1.

Comparing the H function values estimated by using different procedures one can state that these values are very similar. H_{theor} is an average between $\bar{H}_{\mathrm{exp}}$ and

H_{corr}. This confirms that the presented method may be successfully used for estimation of total system non-ideality even in the case of experimental data measured over a limited range of concentrations. The procedure for the evaluation. of $\bar{H}_{exp}$ directly from experimental data is independent of an adsorption model, it only requires an estimation of the adsorption capacity a_m. It characterizes the non-ideality of an adsorption system by a single value, which is stable even in the case of experimental isotherms measured with significant errors. In order to obtain H_{corr} values closer to the theoretical ones, however, it is appropriate to assume an adsorption model; in this case, the simple trapezium approximation may be replaced by a more accurate one when the adsorption model is assumed for this purpose.

References

[1] Jaroniec M. (1983) Adv. Colloid Interface Sci. **18**: 149

[2] House W. A. (1983) In: Everett D. H. (ed.) Specialist periodical reports: Colloid science, vol. 4. Royal Soc. Chem., London, p. 1

[3] Jaroniec M., Madey R. (1988) Physical adsorption on heterogeneous solids. Elsevier, Amsterdam

[4] Rudziński W., Everett D. H. (1991) Adsorption of gases on heterogeneous surfaces. Academic Press, London

[5] Deryło-Marczewska A. (1993) Langmuir **9**: 2344

[6] Marczewski A. W., Jaroniec M., Deryło-Marczewska A. (1986) Mat. Chem. Phys. **14**: 141

[7] Graham D. (1953) J. Phys. Chem. **57**: 665

[8] Müller G., Radke C. J., Prausnitz J. M. (1985) J. Colloid Interface Sci. **103**: 466

[9] Marczewski A. W., Deryło-Marczewska A., Jaroniec M. (1988) Chem. Scripta **28**: 173

[10] Deryło-Marczewska A., Jaroniec M. (1987) In: Matijević E. (ed.) Surface and colloid science, vol. 14. Plenum Press, New York

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