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Description and Estimation of Adsorption from Multicomponent Aqueous Solutions of Dissociating Organic Substances on Activated Carbons

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Summary. The general theoretical description of adsorption from multicomponent dilute aqueous solutions of weak organic electrolytes on solid surfaces is discussed. In the approach, the effect of solution *pH* and ionic strength, and adsorbent energetic heterogeneity is taken into account. The presented model allows to estimate adsorption values in multicomponent systems by using the parameters characterizing single-solute adsorption data. The theoretical discussion is illustrated using new experimental adsorption data for two-component systems consisting of benzoic and salicylic acids over the wide range of *pH* and equilibrium concentrations. The results of adsorption prediction are in good agreement with experiment.

Keywords. Multi-solute adsorption; Adsorption of organic electrolytes; Prediction of multicomponent adsorption.

Beschreibung und Abschätzung der Adsorption aus multikomponenten wäßrigen Lösungen organischer dissoziierender Substanzen auf Aktivkohle

Zusammenfassung. Es wurde eine allgemeine theoretische Beschreibung der Adsorption aus multikomponenten schwachen organische Elektrolyten auf Festkörpen behandelt. In dieser Formulierung wird der Einfluß von *pH* und Ionenstärke der Lösung und die energetische Heterogenität des Adsorbens in Betracht gezogen. Das präsentierte Modell erlaubt die Adsorptionswerte in Multikomponentensystemen mittels Parametern, die für die Adsorption der Einzelkomponenten charakteristisch sind, einzuschätzen. Die Diskussion wird mit neuen experimentellen Daten der Adsorption für Benzoesäure- und Salicylsäure-Mischung in einem weiten Bereich des *pH*-Wertes und der Gleichgewichtskonzentration belegt. Die berechneten Ergebnisse der Adsorption stimmen mit den Experimenten gut überein.

Introduction

In the engineering practice, multicomponent dilute solutions are of great importance. For such systems the problem of their description and prediction is very complicated with regard to a large number of components with various physicochemical properties, which interact and compete to a solid surface. In the case of aqueous solutions of dissociating substances, the effects of other factors: *pH*, ionic strength and their relation to adsorbent surface charge should be taken into account. Considering the fact that experimental measurements of adsorption from multi-solute systems are very time-consuming, the basic problem is to predict the adsorption equilibria in such complicated systems [1–6]. The prediction methods proposed in the literature applied the suitable single-solute data giving quite satisfying agreement with the experiment for the multicomponent system studied. However, in the case of many systems showing strong interactions among components this information may not be sufficient and some additional measurements for mixtures are necessary.

The first attempts to estimate the bi-solute adsorption equilibria by using suitable parameters characterizing the adsorption of single components were connected with the Langmuir isotherm [7–9]. However, with regard to many limitations of this model it can be applied only for some specific systems.

Manes et al. [10, 11] extended the Polanyi potential theory to adsorption from multisolute solutions. The authors found quite good agreement between the experimental and calculated isotherms. The potential theory was also used to consider the *pH* effect on adsorption [12]. In further studies [11] the authors compared the usefulness of their prediction method with the ideal adsorbate solution model (IAS) [13]. The IAS theory applied the thermodynamics of ideal dilute solutions to formulate a procedure for predicting multisolute adsorption by using only the single-solute data. The usefulness of the IAS model for estimation of adsorption from multicomponent systems was reported by many authors [14–16]. The vacancy solution theory first proposed for gas adsorption was adapted to multicomponent dilute solutions [17, 18]. It enables to calculate the multi-solute equilibria using only the data for single-solute adsorption but under the assumption that the adsorbate–adsorbate interactions are negligible. Otherwise, the activity coefficients should be taken into account; they may be obtained from the mixture data or from theoretical considerations.

The next group of predictive methods was based on the theory of physical adsorption on energetically heterogeneous solid surfaces. They were developed by Jaroniec et al. [19–21] and Okazaki et al. [22]. The general idea of this approach is that the isotherm equations for multi-solute adsorption are characterized by the parameters evaluated from the single-solute data. However, these equations were obtained under some mathematical approximations and simplifying assumptions [23]. Müller et al. [24] extended this model for adsorption from multicomponent aqueous solutions of weak organic electrolytes taking into account the effect of solution *pH* and ionic strength. Recently, Marczewski et al. [25, 26] proposed a new method for description of adsorption in multicomponent systems based on the theory of adsorption on heterogeneous solids. It simplifies the mathematical calculations and makes it possible to predict the multicomponent equilibria by using the adsorption data for suitable single-solute systems.

In this paper, a general model of physical adsorption from multi-solute dilute aqueous solutions of dissociating organic substances on energetically heterogeneous solid surfaces is discussed. Its basic assumption is that the adsorption energies for all solution components change in an ordered way. The obtained isotherm equations allow an easier description and prediction of adsorption for multicomponent mixtures. In the approach, adsorbent surface charge established by solution *pH* and ionic strength is also taken into account. The theoretical model is tested with new experimental data for adsorption from dilute aqueous solutions of benzoic and salicyclic acids on activated carbon over the wide range of *pH* and solute concentrations. Adsorption values for bi-component mixtures were estimated using the parameters characterizing adsorption from suitable single-solute systems. Good agreement between the measured and calculated adsorption isotherms was observed.

Theory

Let us consider the adsorption equilibria in a system consisting of dilute aqueous solution of n dissociating organic solutes being in contact with energetically heterogeneous solid surface characterized by surface charge established by solution pH and ionic strength. Some simplifying assumptions are made: all solution components have identical molecular sizes, molecular interactions compensate in adsorbed and bulk phases. Adsorption mechanism in this system is based on competition of organic and water molecules to the surface sites. The inorganic ions (except for H^+ and OH^-) are assumed to form only the diffuse double layer, they do not adsorb on a solid surface. The adsorption process may be described by the solute-solvent exchange reactions, and water is treated as a reference substance "w" = "$n+1$" with constant concentration $x_w^1 \cong 1$ (x_w^1 is the mole fraction of water in the liquid phase). Thus, the basic integral equation describing multi-solute adsorption on a heterogeneous solid may be written as follows [23]

$$\theta_t = \sum_{i=1}^{n} \theta_{i(\mathrm{n})t} = \sum_{i=1}^{n} \int_{\Delta\mathbf{E}} \cdots \int \frac{g_i(c_i, pH, E_i)}{1 + \sum_k^n g_k(c_k, pH, E_k)} \chi(\mathbf{E})\mathrm{d}\mathbf{E}$$

$$= \int_{\Delta\mathbf{E}} \cdots \int \frac{\sum_i^n g_i(c_i, pH, E_i)}{1 + \sum_i^n g_i(c_i, pH, E_i)} \chi(\mathbf{E})\mathrm{d}\mathbf{E}, \tag{1}$$

$$\theta_{i(\mathrm{n})t} = a_{i(\mathrm{n})}/a_{m,i}, \qquad E_i = \varepsilon_i/RT \tag{2}$$

$$\theta_t = \sum_{i=1}^{n} (a_{i(\mathrm{n})}/a_{m,i}) \cong \sum_{i=1}^{n} a_{i(\mathrm{n})}/a_m, \qquad i = 1, 2, \ldots, n.$$

In Eq. (2) $a_{i(\mathrm{n})}$ is the adsorption of the i-th organic solute from the n-component mixture, $a_{m,i}$ is the maximum adsorbed amount for the i-th solute, a_m is the average maximum adsorbed amount, $\theta_{i(\mathrm{n})t}$ is the relative adsorption of the i-th solute onto a heterogeneous solid, θ_t is the total relative adsorption of n solutes, ε_i is the adsorption energy of the i-th solute, E_i is the reduced adsorption energy of the i-th solute, $\Delta\mathbf{E}$ is the n-dimensional energy integration range, c_i is the molar concentration of the i-th solute, $\mathbf{E} = (E_1, E_2, \ldots, E_n)$ is the one-dimensional matrix (i.e. vector) of reduced adsorption energies, $\chi(\mathbf{E})$ is the n-dimensional distribution function of adsorption energies, R is the ideal gas constant, T is the temperature, and $g_i(c_i, pH, E_i)$ is the function depending on adsorption mechanism and describing the local adsorption on the surface patch of constant energy.

With regard to the competition mechanism of adsorption from solutions described by solute-solvent exchange reactions, g_i is a function of values characterizing the solute with respect to water,

$$g_i(c_i, pH, E_i) = g_{i(w)}(x_i^1 c_w, pH, E_{i(w)} - E_w), \tag{3}$$

where x_i^1 is the mole fraction of the i-th component in the bulk phase, c_w is the mole concentration of water and E_w is the adsorption energy of water as solvent.

In the case of dissociating solutes, the adsorption of neutral and ionic forms should be taken into account. Thus, we obtain

$$g_i(c_i, pH, E_i) = g_{is}(c_{is}, E_{is}) + g_{ij}(c_{ij}, pH, E_{ij}), \tag{4}$$

where the subscripts s and j denote the neutral and ionic forms of organic solute.

The concentrations of these forms are related by the dissociation constant pK_a,

$$c_{is} + c_{ij} = c_i, \qquad c_{ij} = f(c_{is}, pH, pK_{ai}).$$

The functions g_i defined by Eqs. (1)–(4) are formulated for the constant value of ionic strength, I. Additionally, we assume that the adsorption of neutral species does not depend directly on the solution pH.

The type of functions g_i depends on the adsorption model assumed, however, their values are connected with the adsorption energy. For non-dissociating solutes we have

$$g_{is}(c_{is}, E_{is}) = K_{is} c_{is}, \tag{5}$$

where K_{is} is the equilibrium constant connected with adsorption energy

$$K_{is} = K_{ios} \exp(E_{is}). \tag{6}$$

K_{ios} is the preexponential factor.

In the case of dissociating substances the electrostatic interactions between the organic ions and charged solid surface have to be taken into account. The model of adsorption description for dilute solutions of dissociating substances proposed by Müller et al. [27] allows to estimate the effect of solution pH and ionic strength, and surface energetic heterogeneity on adsorption equilibria. Following the considerations presented in Ref. [27] in terms of the electrostatic theory and the classical Gouy–Chapman model of electrical double layer, we may write the function g_i as follows,

$$g_{ij}(c_{ij}, pH, E_{ij}) = K_{ij} f_q c_{ij}, \tag{7}$$

where

$$K_{ij} = K_{ioj} \exp(E_{ij}), \tag{8}$$

$$f_q = \exp(-z_{i\pm} F \phi_s / RT). \tag{9}$$

The constant K_{ij} describes the ion adsorption on an electrically neutral surface, however, the factor f_q reflects the effect of solid surface charge on the adsorption process. In Eq. (9) $z_{i\pm}$ is the charge of the organic ion, F is Faraday's constant and ϕ_s is the electric interfacial potential. With regard to the condition of system electroneutrality, the surface charge density, $q_s = q_s(pH, I)$ should be balanced by the charge density due to all adsorbed ions, $q_a = q_a(\theta_t^{(j)}) = (a_m F / S_{\mathrm{BET}}) \theta_t^{(j)}$ ($\theta_t^{(j)}$ is the relative adsorption of all adsorbed ions) and by the charge density of diffuse double layer, $q_d = q_d(\phi_s)$,

$$q_s + q_a + q_d(\phi_s) = 0. \tag{10}$$

However, the relation $q_d(\phi_s)$ has the following form,

$$-z_d q_d = \sqrt{8\varepsilon RTI} \sinh\left(\frac{|z_d| \phi_s F}{2RT}\right), \tag{11}$$

where $z_d = |z_+| = |z_-|$ is the valence of ions in diffuse layer, ε is the solution dielectric permittivity, I is the ionic strength $I = (1/2)\sum_i c_i z_i^2$ and S_{BET} is the BET surface area.

The species forming the diffuse double layer determine the electrical potential difference between solid surface and liquid phase. The $\phi_s(q_s, I)$ value may be determined from Eqs. (10) and (11). The surface charge density q_s is determined from the experimental data of potentiometric titration.

The integral equation (1) may be solved analytically or numerically under some specific assumptions for various distribution functions of adsorption energies and different forms of functions g_i [6, 23]. As a result, one can obtain the isotherms for multi-solute adsorption containing the parameters characterizing the single-solute equilibria. They may be used to estimate the values of adsorption from multicomponent systems. In Ref. [25] a new method of description of adsorption equilibria for multicomponent systems was presented. It was based on the assumption of an ordered manner of adsorption energy changes for solution components. Thus, a certain correlation exists between the adsorption energies of solutes "i" and "k",

$$E_i = E_i(E_k) \qquad \text{and} \qquad E_k = E_k(E_i), \qquad i = 1, 2, \ldots, n. \tag{12}$$

This means, if the molecules of the i-th and k-th component adsorb on the surface site "$*$", their adsorption energies and distribution functions are related as follows,

$$\int_{E^*_{i,\min}}^{E_i^*} \chi(E_i)\mathrm{d}E_i = \int_{E^*_{k,\min}}^{E_k^*} \chi_k(E_k)\mathrm{d}E_k = F(E_i^*) = F(E_k^*) = F^*, \tag{13}$$

where $F(E_i) \in \langle 0, 1 \rangle$ is the integral distribution function which is connected with the differential distribution function χ,

$$\frac{\mathrm{d}F}{\mathrm{d}E_i} = \chi(E_i). \tag{14}$$

The conditions (12) and (13) denote that the same tendency of adsorption energy – increasing or decreasing – is observed for all solution components and for all surface sites.

After introducing the assumptions (12) and (13) to the integral equation (1) a transformation of the n-dimensional integral to a one-dimensional one is possible,

$$\theta_t = \int_0^1 \frac{\sum_i^n g_i[c_i, pH, E_i(F)]}{1 + \sum_i^n g_i[c_i, pH, E_i(F)]} \mathrm{d}F, \tag{15}$$

and then for a new variable describing the distance of adsorption energy from the mean energy

$$z_i(F) = E_i(F) - \bar{E}_i \tag{16}$$

we obtain:

$$\theta_t = \int_0^1 \frac{\sum_i^n \bar{g}_i(c_i, pH, \bar{E}_i)\exp[z_i(F)]}{1 + \sum_i^n \bar{g}_i(c_i, pH, \bar{E}_i)\exp(z_i(F)]} \mathrm{d}F, \tag{17 a}$$

$$\theta_{i(n)t} = \int_0^1 \frac{\bar{g}_i(c_i, pH, \bar{E}_i)\exp[z_i(F)]}{1 + \sum_k^n \bar{g}_k(c_k, pH, \bar{E}_k)\exp[z_k(F)]} \mathrm{d}F, \tag{17 b}$$

where

$$\bar{g}_i = g_i(c_i, pH, \bar{E}_i) = \bar{g}_{is}(c_{is}, \bar{E}_{is}) + \bar{g}_{ij}(c_{ij}, pH, \bar{E}_{ij}) = \bar{K}_{is}c_{is} + \bar{K}_{ij}K_q c_{ij}, \tag{18}$$

$$\bar{K}_{is} = K_{ios}\exp(\bar{E}_{is}), \qquad \bar{K}_{ij} = K_{ioj}\exp(\bar{E}_{ij}). \tag{19}$$

The energy distribution function is described by the mean adsorption energy $\bar{E}$,

$$\bar{E}_i = \int_0^1 E_i(F)\mathrm{d}F = \int_{\Delta E_i} E_i\chi(E_i)\mathrm{d}E_i, \tag{20}$$

and the energy dispersion, σ, which characterizes the heterogeneity effects:

$$\sigma_i^2 = \int_0^1 [E_i(F) - \bar{E}_i]^2\mathrm{d}F = \int_{\Delta E_i} (E_i - \bar{E})^2\chi(E_i)\mathrm{d}E_i. \tag{21}$$

The isotherm equation (17) describing the adsorption from the n-component mixture has a simpler form than the integral equation (1). It is characterized by the functions $z_i(F)$ and the mean energy constants $\bar{K}_i$ obtained from the experimental data of single-solute adsorption. Thus, Eq. (17) may be useful for predicting the parameters of multicomponent adsorption.

In the case of solutions containing n components showing similar adsorptive properties we may assume that the distribution functions corresponding to different solutes have the same shape and they are only shifted on the energy axis. It means that their distributions are identical $z_i(F) = z(F)$, however, their mean energies $\bar{E}_i$ are different. Thus, it is possible to simplify the isotherm (17):

$$\theta_t = \int_0^1 \frac{[\sum_i^n \bar{g}_i(c_i, pH, \bar{E}_i)]\exp[z(F)]}{1 + [\sum_i^n \bar{g}_i(c_i, pH, \bar{E}_i)\exp[z(F)]}\mathrm{d}F, \tag{22 a}$$

$$\theta_{i(\mathbf{n})t} = \int_0^1 \frac{\bar{g}_i(c_i, pH, \bar{E}_i)\exp[z(F)]}{1 + [\sum_k^n \bar{g}_k(c_k, pH, \bar{E}_k)]\exp[z(F)]}\mathrm{d}F. \tag{22 b}$$

Thus, for any i-th and p-th solutes we obtain

$$\theta_{i(\mathbf{n})t}/\theta_{p(\mathbf{n})t} = \bar{g}_i(c_i, pH, \bar{E}_i)/\bar{g}_p(c_p, pH, \bar{E}_p), \qquad i, p = 1, 2, \ldots, n. \tag{22 c}$$

Competition between solution components is an important feature of liquid adsorption. The above isotherm equations were based on the solute-solvent exchange reactions. However, for high solute surface coverages, the role of solvent diminishes and the adsorption process may be described by the competition between solute molecules. Thus, the adsorption equilibrium may be expressed in terms of adsorption energy differences between the i-th solute and a reference solute "n",

$$\theta_t = \textstyle\sum_{i=1}^n \theta_{i(\mathbf{n})t} \cong 1 \tag{23 a}$$

and

$$\theta_{i(\mathbf{n})t} \cong \int_0^1 \frac{\bar{g}_{in}(c_{in}, pH, \bar{E}_{in})\exp[z_{\mathrm{in}}(F)]}{1 + [\sum_k^{n-1} \bar{g}_{kn}(c_{kn}, pH, \bar{E}_{kn})]\exp[z_{kn}(F)]}\mathrm{d}F. \tag{23 b}$$

When $|z_{in}(F)| \ll |z_n(F)|$ we have

$$\theta_{i(\mathbf{n})t}/\theta_{p(\mathbf{n})t} \cong \bar{g}_i(c_i, pH, \bar{E}_i)/\bar{g}_p(c_p, pH, \bar{E}_p). \tag{23 c}$$

In the above,

$$\bar{g}_{in} = \bar{g}_i/\bar{g}_n, \qquad z_{in}(F) = z_i(F) - z_n(F), \qquad \bar{E}_{in} = \bar{E}_i - \bar{E}_n. \tag{24}$$

Experimental

Experimental adsorption isotherms were measured for the mixtures of benzoic and salicylic acids contacted with the experimental granular activated carbon RIC from Norit n.v. (Amersfoort, Netherlands) at 293 K. Prior to experiment the activated carbon was dried at 120 °C; its characteristics are as follows: $S_{\mathrm{BET}} = 990 \pm 30\,\mathrm{m}^2/\mathrm{g}$, total specific pore volume $V_p = 0.59\,\mathrm{cm}^3/\mathrm{g}$. Its surface charge was determined by potentiometric titration for the ionic strength $I = 0.01$ and $0.1\,\mathrm{mol/l}$. The adsorbate solutions were prepared of bi-distilled water and benzoic ($pK_a = 4.2$ at 293 K) and salicylic ($pK_{a1} = 2.98$, $pK_{a2} = 13.82$) acids of commercially available quality.

The adsorption isotherms were measured for the constant ionic strength $I = 0.1\,\mathrm{mol/l}$ and over the pH range 2.1–10.5. The ionic strength was established by addition of NaCl, and the pH by addition of HCl and NaOH solutions. The isotherms were established under the constant initial concentration of one component: 0, 2, 4, 6, 8 and 10 mmol/l. In order to choose the measured concentration range in the best possible manner and to obtain the definite equilibrium pH, the simulation procedure was elaborated. The compositions of adsorbate solutions and activated carbon amounts were prepared according to the simulated theoretical isotherms.

After attaining equilibrium, the solute concentrations were measured by using the UV–VIS spectrophotometer Specord M40 (Carl Zeiss, Jena). The solute adsorbed amount was then calculated using the material balance. Details of the experimental procedure were described in Ref. [28].

Results and Discussion

In order to investigate the usefulness of the proposed method for estimation of adsorption value for multicomponent systems, we analysed the experimental data of bi-solute adsorption from dilute aqueous solutions: benzoic acid (1) + salicylic acid (2), by using parameters characterizing the suitable single-solute adsorption systems [28]. The single-solute adsorption isotherms were analysed using the following form of Eq. (17 b),

$$a_{i(1)}/a_m = \theta_{i(1)t} = \int_0^1 \frac{\bar{g}_i(c_i, pH, \bar{E}_i)\exp[z_i(F)]}{1 + \bar{g}_i(c_i, pH, \bar{E}_i)\exp[z_i(F)]}\,\mathrm{d}F, \qquad i = 1, 2, \tag{25}$$

where the function $\bar{g}_i$ is expressed by Eq. (18).

The interfacial electric potential ϕ_s was calculated from Eqs. (10) and (11). The Gauss distribution function of adsorption energies was assumped to characterize the system heterogeneity

$$F(z) = \frac{1}{2}\left[1 + \mathrm{sign}(z)\,\mathrm{erf}\left(\left|\frac{z}{\sqrt{2}\sigma}\right|\right)\right]. \tag{26}$$

The calculations were performed under the assumption of equality of adsorption capacity $a_m = 4.7\,\mathrm{mmol/g}$ for both systems considered and its value was estimated from the BET surface area and the average area occupied by simple aromatic molecule ($0.35\,\mathrm{nm}^2/\mathrm{g}$). The values of parameters of Eq. (25) for both single-solute systems were evaluated using the optimization procedure utilizing the optimization package MINUIT (CERN, Geneve). The details of these calculations and their results were presented in Ref. [28]. In Table 1 the best-fit parameters characterizing adsorption of benzoic (1) and salicyclic (2) acids from dilute aqueous solutions on activated carbon RIC are presented.

The parameters characterizing single-solute adsorption presented in Table 1 were then applied to estimate the value of adsorption from bi-solute aqueous

Table 1. Parameters of Eq. (25) characterizing adsorption of benzoic (1) and salicylic (2) acids from dilute aqueous solutions on activated carbon RIC at 293 K ($a_m = 4.7\,\mathrm{mmol/g}$)

Single solute	$\lg \bar{K}_s$[a]	$\lg \bar{K}_j$[a]	σ_i	SD[a]
Benzoic acid (1)	0.196	−1.705	4.75	0.0263
Salicylic acid (2)	0.713	−0.828	5.12	0.0284

[a] $\bar{K}_s$ and $\bar{K}_j$ in [l/mmol], $\mathrm{SD} = [\sum_{l=1}^{L} (\lg a_{\mathrm{opt},l} - \lg a_{\mathrm{exp},l})^2/(L-4)]^{1/2}$, L = number of exp. points

solutions of benzoic (1) + salicylic (2) acids over a wide pH range. The calculations were performed for Eq. (17 b):

$$a_{i(2)}/a_m = \theta_{i(2)t} = \int_0^1 \frac{\bar{g}_i(c_i, pH, \bar{E}_i)\exp[z_i(F)]}{1 + \sum_{k=1}^{2} \bar{g}_k(c_k, pH, \bar{E}_k)\exp[z_k(F)]}\,\mathrm{d}F, \qquad i = 1, 2. \quad (27)$$

In the numerical procedure the values of partial adsorption $a_{1(2)}$, $a_{2(2)}$ and the total summaric adsorption $a_{1+2(2)}$ were estimated. With regard to the specific character of multicomponent adsorption isotherms it is difficult to present graphically the data measured for a wide range of pH and concentrations. In the paper, in order to show the applicability and correctness of optimization [28] and prediction procedures, the comparison of experimental (exp), optimized (opt) (single-solute data), and predicted (pre) (bi-solute data) adsorption values is presented in Figs. 1–3. Two different plots are used: adsorption vs. adsorption and lg(adsorption) vs. lg(adsorption). The first dependence allows to estimate the quality of optimization

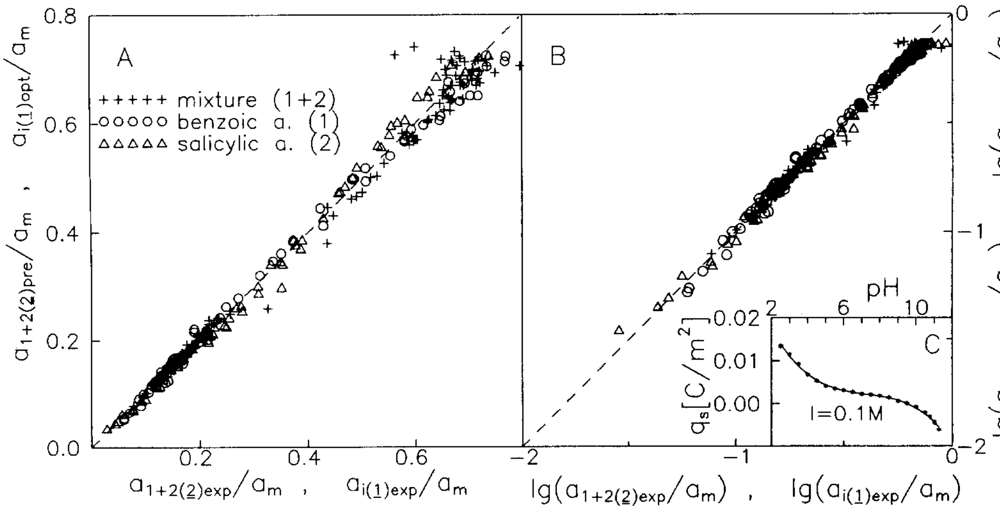

Fig. 1. Comparison of the experimental, optimized (for single-solute adsorption) and predicted (summaric values for bi-solute adsorption) adsorption values for aqueous solutions of benzoic acid (1), salicylic acid (2) and their mixtures over the pH range 1.3–10.5 (parts A, B); the dependence $q_s = f(pH)$ determined from the potentiometric titration data for $I = 0.1\,\mathrm{mol/l}$ is given in part C (inserted in B)

and prediction for the range of intermediate and high adsorption values. However, the log-log plot makes it possible to appreciate the fitting quality for low adsorption values. Thus, both plots used together allow to estimate generally the quality of optimization and prediction over the whole range of measured *pH* and adsorption.

In Fig. 1 the experimental data for single-solute and bi-solute (total adsorption) adsorption are compared with the optimized (Eq. (25)) and predicted (Eq. (27)) adsorption values, respectively. The presented data cover the whole range of measured *pH* values. In Fig. 1C the experimental dependence of surface charge density q_s on *pH* obtained by potentiometric titration is drawn. Figure 2 presents the comparison of experimental and predicted values of partial adsorption for the bi-solute system. The points are grouped in three narrow *pH* ranges. However, in Fig. 3 the predicted values of total summaric adsorption of benzoic (1) + salicylic (2)

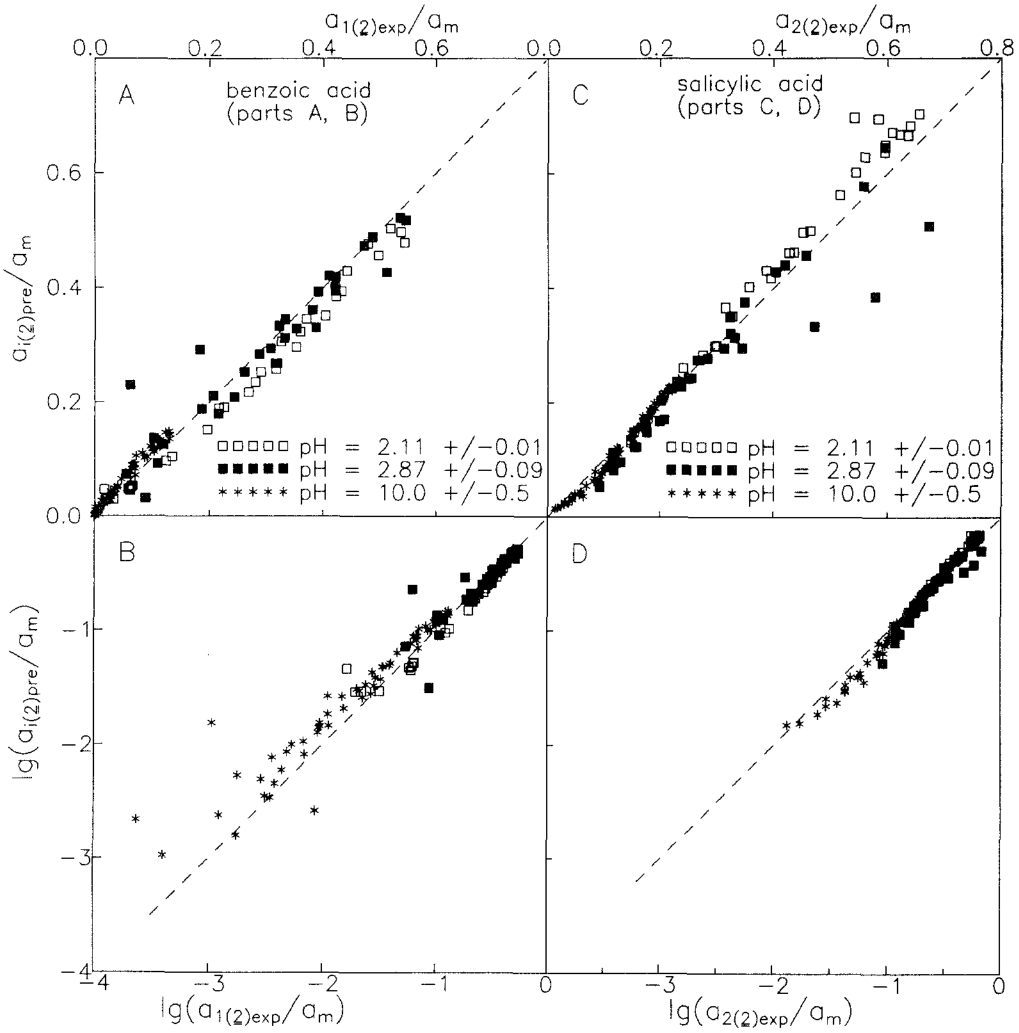

Fig. 2. Comparison of the experimental and predicted partial adsorption values of benzoic (1) and salicylic (2) acids from their mixture for different *pH* values; the dependence $q_s = f(pH)$ is presented in Fig. 1C

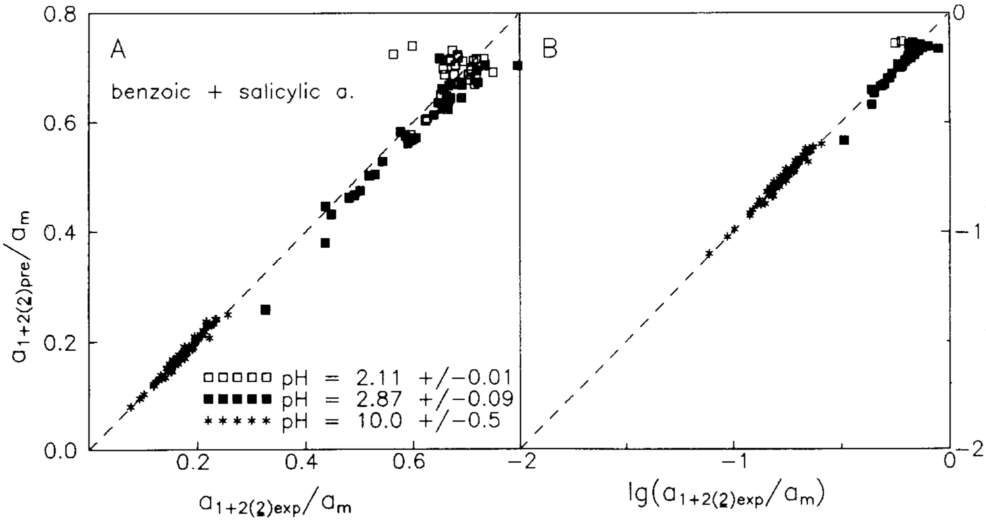

Fig. 3. Comparison of the experimental and predicted values of total summaric adsorption for aqueous solutions f benzoic (1) + salicylic (2) acids for different *pH* values the dependence $q_s = f(pH)$ is presented in Fig. 1C

Table 2. Deviations of predicted from experimental adsorption values for the bi-solute system: benzoic acid (1) + salicylic acid (2) (128 experimental points) ($\mathrm{SD}(y) = [\sum_{l=1}^{L} (y_{\mathrm{pre},l} - y_{\mathrm{exp},l})^2/(L-4)]^{1/2}$, L = number of exp. points)

Solute	SD formula	SD value
Benzoic acid (1)	$\mathrm{SD}(\theta_i)$	0.03033
	$\mathrm{SD}(\lg\theta_i)$	0.20582
Salicylic acid (2)	$\mathrm{SD}(\theta_i)$	0.03864
	$\mathrm{SD}(\lg\theta_i)$	0.07297
Benzoic (1) + salicylic (2) acids	$\mathrm{SD}[\lg(\sum_i^n \theta_i)]$	0.02672

acids are compared with the suitable experimental data. Good agreement between the experimental points and predicted dependences observed for all studied systems confirms the usefulness and correctness of the model presented. In Table 2 the deviations of predicted adsorption values from experimental data are given. The relatively high SD values for partial isotherms are caused by some of the experimental points showing low adsorption values for at least one solute. The experimental errors are connected with worse precision of UV–VIS measurements being a result of spectral interferences and very low absorption values for low solute concentrations.

For the bi-solute systems consisting of two components with similar adsorptive properties ($\sigma_1 \cong \sigma_2$) we have

$$a_{1(2)}/a_{2(2)} = \theta_{1(2)t}/\theta_{2(2)t} = \bar{g}_1(c_1, pH, \bar{E}_1)/\bar{g}_2(c_2, pH, \bar{E}_2). \qquad (28)$$

In the case of non-dissociating compounds the adsorption equilibrium may then be described only in terms of the mean adsorption energy differences by the following linear form of Eq. (28),

$$\lg(a_{1(2)}/a_{2(2)}) = \lg \bar{K}_{12s} + \lg c_{12}, \qquad (29)$$

$$\bar{K}_{12s} = \bar{K}_{1s}/\bar{K}_{2s}, \qquad c_{12} = c_1/c_2.$$

However, for the systems consisting of dissociating solutes the form of dependences (28), (29) becomes more complicated because of the effect of surface charge

$$\lg(a_{1(2)}/a_{2(2)}) = \lg c_{12} + \lg \bar{K}_{12s} + \lg\left(\frac{1 + 10^{pK_{a2} - pH}}{1 + 10^{pK_{a1} - pH}}\right) + (pK_{a1} - pK_{a2})$$

$$+ \lg\left[\frac{1 + (K_{1j}/K_{1s})10^{pH - pK_{a1}} f_q(pH, c_1, c_2)}{1 + (K_{2j}/K_{2s})10^{pH - pK_{a2}} f_q(pH, c_1, c_2)}\right]. \qquad (30)$$

Generally, the isotherm (30) may be written as follows,

$$\lg(a_{1(2)}/a_{2(2)}) \cong \lg \bar{K}_{12}(pH) + \lg c_{12}, \qquad (31)$$

where

$$\lg \bar{K}_{12}(pH \ll pK_{a1}, pK_{a2}) = \lg \bar{K}_{12s},$$

$$\lg \bar{K}_{12}(pH \gg pK_{a1}, pK_{a2}) = \lg \bar{K}_{12j},$$

where K_{a1} is the dissociation constant for solute "i". With regard to the dependence of f_q on solute concentrations, the linear character of Eq. (29) is not strictly kept for solutions of weak electrolytes, however, it may be treated as an approximate relation.

In the case of solutes showing greater differences in their adsorptive behaviour the effect of surface heterogeneity should be also taken into account (for simplicity, the influence of electrostatic interactions is neglected),

$$\lg(a_{1(2)}/a_{2(2)}) \cong m \lg \bar{K}_{12}(pH) + m \lg c_{12}, \qquad (32)$$

where the parameter m is a function of adsorption energy dispersions $m = f(\sigma_1, \sigma_2)$. For the systems consisting of solutes with well correlated adsorption energies, especially for a linear dependence $E_1 = \alpha E_2 + \beta$, dispersion of energy differences $E_{12} = E_1 - E_2$ is equal to $\sigma_{12} = |\sigma_1 - \sigma_2|$, and one obtains $m \cong f(\sigma_{12}) = f(\sigma_1 - \sigma_2)$. On the contrary, for the systems with negative linear correlation ($E_1 = -\alpha E_2 + \beta$), we have $\sigma_{12} = \sigma_1 + \sigma_2$. However, in the case of systems showing no energy correlation we obtain $\sigma_{12}^2 = \sigma_1^2 + \sigma_2^2$ and the dependence shown in Eq. (32) may not be linear (25), (26).

As it was stated above, the investigated system may be well described in terms of adsorption energy differences, $E_{12} = E_1 - E_2$, with dispersion $\sigma_{12} = |\sigma_1 - \sigma_2|$. In the case of the analysed experimental system we have $\sigma_{12} = 0.37$. Let us consider the bi-solute system under the condition of full surface coverage ($\theta_1 + \theta_2 = 1$) (Eq. 27)) which can be also described as follows,

$$\lg(\theta_1/\theta_2) = \lg[\theta_1/(1 - \theta_1)] \cong m \lg \bar{K}_{12}(pH) + m \lg c_{12}. \qquad (33)$$

The values of parameters characterizing the linear dependence (33) for the theoretical adsorption isotherm corresponding to the Gauss distribution function with $\sigma_{12} = |\sigma_1 - \sigma_2| = 0.37$ were calculated under the assumption of lack of dissocia-

Table 3. Parameters of the linear plot (33) corresponding to the model isotherm (27) with Gauss distribution of adsorption energies ($a_m = 1$, $\bar{K}_{12} = 1$, $\sigma_{12} = 0.37$) and $\theta_1 + \theta_2 = 1$

Range of $\lg \theta_{12}$	m	$m \lg \bar{K}_{12}$
$(-3, 3)$	0.9850 ± 0.0009	-0.002 ± 0.007
$(-2, 2)$	0.9804 ± 0.0008	-0.0008 ± 0.0041

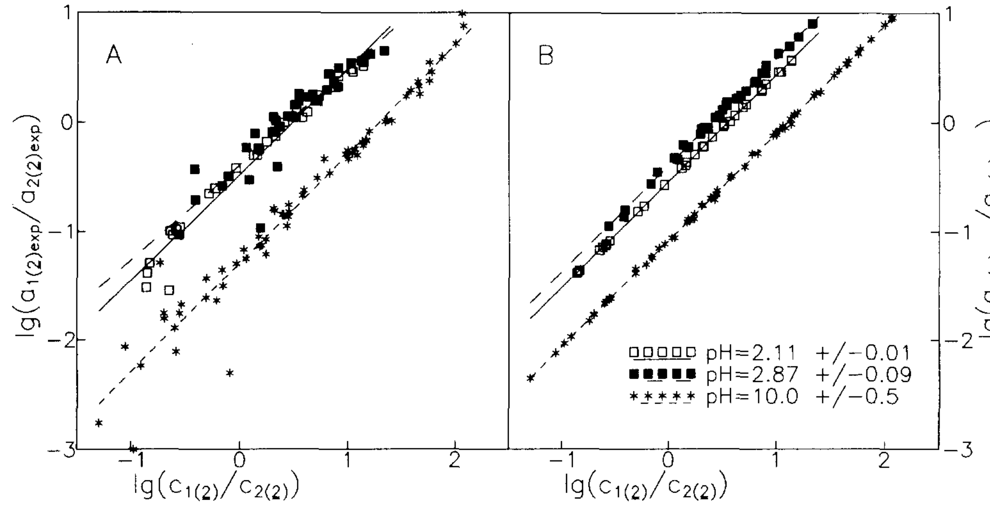

Fig. 4. Comparison of the experimental $\lg(a_{1(2)\mathrm{exp}}/a_{2(2)\mathrm{exp}})$ vs. $\lg(c_{1(2)}/c_{1(2)})$(A) and predicted dependences $\lg(a_{1(2)\mathrm{pre}}/a_{2(2)\mathrm{pre}})$ vs. $\lg(c_{1(2)}/c_{1(2)})$(B) for adsorption from the aqueous solutions of benzoic (1) + salicylic (2) acids for different *pH* values; the dependence $q_s = f(pH)$ is presented in Fig. 1C

tion effects ($a_m = 1$, $\bar{K}_{12} = 1$). These values are presented in Table 3 for two ranges of equilibrium concentrations and adsorptions: $\lg(\theta_1/\theta_2) \in (-2, 2)$ and $(-3, 3)$.

In order to confirm the assumed linear correlation between adsorption energies (Eqs. (12), (13)) the experimental and predicted data were plotted in the coordinates of Eqs. (29)–(32). The straight lines drawn in Fig. 4 are the best-fit lines. These dependences have pure experimental character, they do not require any assumptions or former interpretations. The figure evidences univocally the competitive adsorption mechanism with a good correlation of adsorption energies of solutes. In Table 4 the parameters of linear dependences (29)–(32) are given. The slopes of straight lines presented in Fig. 4 are contained over the range 0.98–1.0 (except for $pH = 2.87$) what corresponds to a little difference of dispersion energies [26]. The parameter values presented in Table 4 confirm the assumption of similarity of adsorptive properties for solution components over the whole studied range of measured *pH*. It means that the assumption about a strong correlation of adsorption energies for solution components made in Eqs. (12), (13) is reasonable for the analysed systems. The slopes found from experimental dependences (Fig. 4A) (Table 4) are in very good agreement with the values found for the theoretical isotherm Eq. (27) (Fig. 4B)

Table 4. Parameters of linear dependences (29–32) presented in Fig. 4

pH	m_{exp} (m_{pre})	$m \lg \bar{K}_{12\mathrm{exp}}$ ($m \lg \bar{K}_{12\mathrm{pre}}$)	SD
2.11 ± 0.01	0.975 (0.978)	0.476 (0.538)	0.110 (0.007)
2.87 ± 0.09	0.875 (0.980)	0.388 (0.390)	0.185 (0.026)
10.0 ± 0.5	1.002 (0.980)	1.290 (1.080)	0.204 (0.017)

(Table 4) and with the slopes calculated from Eq. (33) ($\theta_1 + \theta_2 = 1$, $\sigma_{12} = |\sigma_1 - \sigma_2|$, Eq. 27) (Table 3) for linearily correlated energies of the components.

Comparing the dependences presented in Figs. 4A and 4B one can find certain differences in their course. They result first from the dispersion of experimental points and from the approximation of a real system by a theoretical model. The next reason is that the dependences in Fig. 4B were predicted using optimized parameters for single-solute adsorption without any correction for multi-solute data.

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