

Adsorption of Organics from Aqueous Solutions on Microporous Carbons

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Introduction

The adsorption on activated carbons from dilute aqueous solutions of organic substances has a great practical importance [1-3]. The studies of such systems, especially those containing larger number of solutes, are very complex. The necessity of taking into consideration the effect of many factors on adsorption equilibria: the structural and energetic heterogeneity of an adsorbent, the differences in physicochemical properties of adsorbates, and the electrostatic and lateral interactions in adsorbed phase makes it a very difficult problem [2,4-8]. The analysis of these systems becomes more intricate with the increase of number of adsorbed species. In the literature several methods were proposed for the description of adsorption from multicomponent systems [6-15]. The first simple model was proposed by Langmuir [16]. Most theoretically advanced approaches were discussed in terms of various models, e.g. the extension of Polanyi's potential theory [9], the ideal adsorbate solution (IAS) model [10,11], the vacancy solution model [12], the theory of adsorption on energetically heterogeneous surfaces [2,4-8,13,14].

In this paper the process of adsorption of organic substances from aqueous solutions on activated carbon is considered. The experimental data of mixed adsorption data are presented and analysed on the ground of the theory of physical adsorption on energetically heterogeneous solids. This model allows a simple evaluation of the effect of many factors on adsorption equilibria, including the ionisation of solutes. In order to focus on the solute type and heterogeneity effects, the solution pH was fixed at the values practically preventing solute ionisation. The study of influence of pH on solute adsorption was published elsewhere [5,7].

Experimental

The experimental isotherms were measured for adsorption of single organics and their mixtures from dilute aqueous solutions on the granular activated carbon RIC (Norit n.v., Amersfoort, Netherlands) at 293 K. In order to remove some inorganic impurities the activated carbon was washed with acids and rinsed with bidistilled water. The carbon properties were determined from nitrogen adsorption isotherm: the specific surface area $S_{BET}=975$ m²/g and the total pore volume $V_p=0.59$ cm³/g. Prior to experiment the activated carbon was dried at 393 K.

The adsorption isotherms were measured for the constant ionic strength $I=0.1$ mol/l and pH=2.2. The adsorbate solutions were prepared with bidistilled water and organic substances of commercially available quality. Benzoic acid (pK_a=4.2), salicylic acid (pK_a=2.98), 4-nitrophenol (pK_a=7.25) and 4-nitrotoluene were used as adsorbates. Before contacting with adsorbate solution a known amount of activated carbon was added to 5 ml of bidistilled water and the mixture was degassed under vacuum in order to remove the air from the pores. The amount of water removed during the process was controlled. The ionic strength

was established by adding NaCl, and pH was established by addition of HCl solution. The isotherms for bi-solute systems were established under the constant initial concentration of one component: 1, 2 and 3 mmol/l. In order to obtain the definite equilibrium pH and to choose the measured concentration range in the best possible manner, the simulation procedure was elaborated [17]. The theoretical isotherms of Langmuir type were simulated for the assumed approximate parameters. The surface charge of activated carbon and the charge due to adsorbed organic ions and their relation to pH changes during adsorption process were taken into account in the simulation procedure. The compositions of adsorbate solutions and activated carbon amounts were prepared according to the simulated theoretical isotherms. After equilibrium was attained, the solute concentrations were measured by using the UV-vis spectrophotometer Specord M-40 (Carl Zeiss, Jena, Germany). The amount of adsorbed organic substance was calculated from the experimental data using the material balance:

$$a = \frac{V(c_o - c)}{m_{ad}} \quad (1)$$

In the above, a is the solute adsorption, V is the solution volume, m_{ad} is the adsorbent mass, c_o is the initial solute concentration, and c is its equilibrium concentration.

Results and discussion

The experimental adsorption isotherms from binary solutions of benzene derivatives on the activated carbon RIC were measured under the constant initial concentration of the first component (1, 2 and 3 mmol/l) for the following systems:

benzoic acid (1) + 4-nitrotoluene (2) (BA-4NT)

salicylic acid (1) + 4-nitrotoluene (2) (SA-4NT)

4-nitrophenol (1) + 4-nitrotoluene (2) (4NP-4NT).

These isotherms are presented in Figs. 1-3.

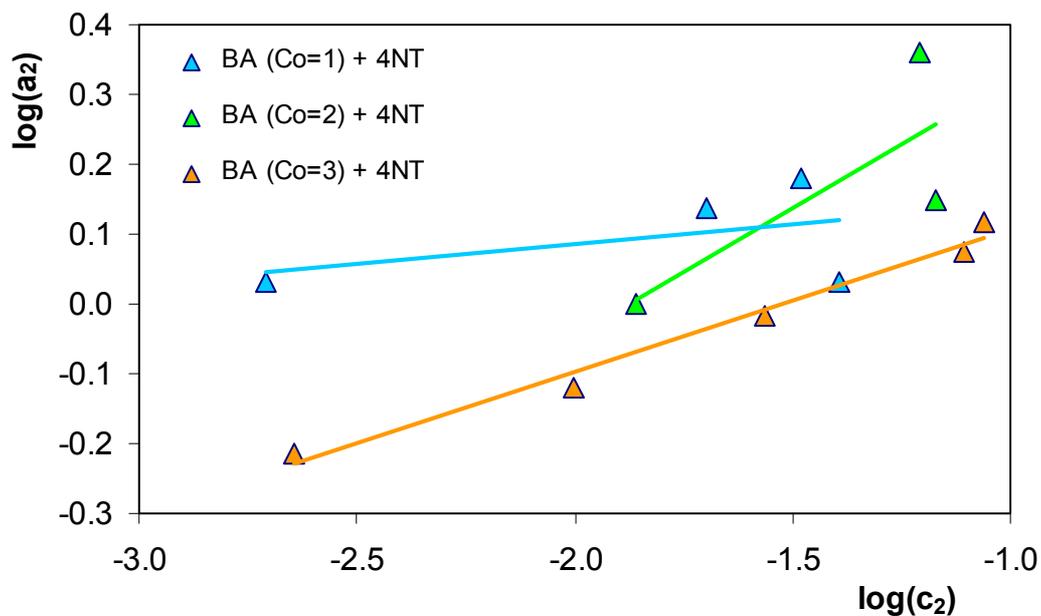


Fig.1. The adsorption isotherms of 4-nitrotoluene (4NT) (2) measured under constant initial concentration (c_o [mmol/l]) of benzoic acid (BA) (1) from bi-component dilute aqueous solutions on the activated carbon RIC at 293 K.

species with a solid, and the adsorbate structure. Here, one must distinguish between the heterogeneity found for single solute adsorption systems (competition of solute and solvent) and heterogeneity effects observed in the competitive adsorption of binary solute systems (for high surface coverages – describing competition of solutes). For example, in the case of studied systems, greater heterogeneity effects for solute competitive adsorption were observed for adsorption of 4NP-4NT as contrasted to (BA-4NT) and (SA-4NT). It is apparently related to the highest divergence of functional groups for 4NP and 4NT *versus* adsorbent, what results in higher differentiation of adsorption energies.

First, the known Langmuir-Freundlich isotherm equation was used for the analysis of experimental data in the following linear form [2,4]:

$$\log(\theta_1 / \theta_2) = \log(a_1 / a_2) = m \log \bar{K}_{12} + m \log(c_1 / c_2) \quad (2)$$

In the above, θ_i ($i=1,2$) is the surface coverage for solute “i”, a_i is the solute adsorption, c_i is the solute concentration, $m \in (0, 1 >$ is the heterogeneity parameter characterizing the shape of the energy distribution function, and \bar{K}_{12} is the ratio of solute equilibrium constants describing the position of the adsorption energy function on the energy axis.

The linear dependences (2) are drawn in Fig. 4, however, the values of parameters characterizing the studied experimental systems are compared in Table 1.

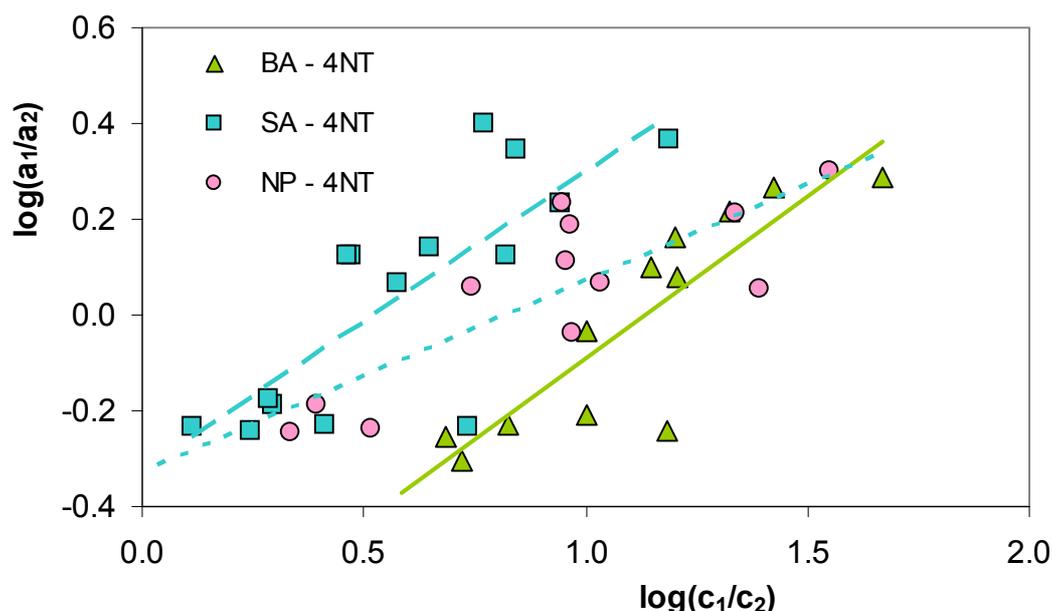


Fig.4. The linear dependencies (2) for adsorption from bi-component dilute aqueous solutions of organic substances on the activated carbon RIC at 293 K.

Table 1. The values of parameters characterising adsorption from bi-component dilute aqueous solutions of organic substances on activated carbon RIC at 293 K.

Adsorption System	m	$\log \bar{K}_{12}$
Benzoic acid (1) + 4-Nitrotoluene (2)	0.67	-1.14
Salicylic acid (1) + 4-Nitrotoluene (2)	0.62	-0.52
4-Nitrophenol (1) + 4-Nitrotoluene (2)	0.40	-0.82

Let us consider the values of heterogeneity parameters collected in Table 1. In the case of all studied adsorption systems rather strong non-homogeneity effects are observed. The

lowest value (the highest heterogeneity effects) of this parameter is found for the system 4-nitrophenol (1) + 4-nitrotoluene (2). It is connected with the differentiation of 4-nitrophenol (two different functional groups interacting in a different way with carbon surface) structure in comparison to benzoic and salicylic acids. The values of equilibrium constants \bar{K}_{12} are related to the difference of adsorption energies for solutes “1” and “2”. In the case of all studied experimental systems these values are lower than zero, thus 4-nitrotoluene is adsorbed stronger than the other organics.

Besides the heterogeneity effects the differences of sizes of adsorbate molecules influence significantly the adsorption process. Taking into account both factors we obtain the following linear equation [2]:

$$\log(a_1/c_1) = \log \bar{K}_{12} + r \log(a_2/c_2) \quad (3)$$

In Fig. 5 the experimental isotherms for three chosen systems are drawn in the coordinates $\log(a_1/c_1)$ vs. $\log(a_2/c_2)$. Good correlation is observed for all adsorption systems. The parameters of these linear equations are compared in Table 2 (r is the ratio of solute sizes in adsorbed phase – optimised parameters, whereas V_{m1}/V_{m2} is the ratio of molar volumes for substances “1” and “2”). The value of parameter r is quite close to unity for adsorption systems: SA–4NT and NP–4NT. For BA–4NT system it takes lower value. However, all optimised values are close to the ratios of molar volumes of pure adsorbates.

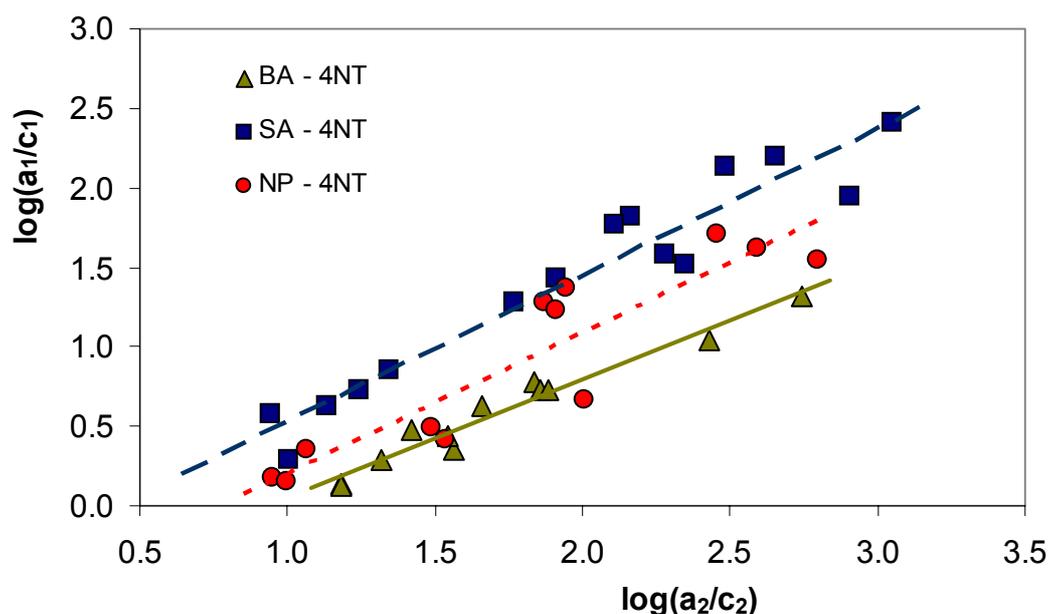


Fig.5. The linear dependencies (3) for adsorption from bi-component dilute aqueous solutions of organic substances on the activated carbon RIC at 293 K.

Table 2. The values of parameters characterising adsorption from bi-component dilute aqueous solutions of organic substances on activated carbon RIC at 293 K.

Adsorption System	V_{m1}/V_{m2}	r	$\log \bar{K}_{12}$
Benzoic acid (1) + 4-Nitrotoluene (2)	0.82	0.74	-0.68
Salicylic acid (1) + 4-Nitrotoluene (2)	0.81	0.92	-0.39
4-Nitrophenol (1) + 4-Nitrotoluene (2)	0.80	0.88	-0.88

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