Nonhomogeneity Effects in Adsorption from Gas and Liquid Phases on Activated Carbons

A. Derylo-Marczewska* and A. W. Marczewski

Faculty of Chemistry, Maria Curie-Skłodowska University, 20031 Lublin, Poland

Received January 12, 1999. In Final Form: March 22, 1999

The process of adsorption of dissociating organic substances from dilute aqueous solutions on various activated carbons is studied. The investigated adsorbents have different pore structure and chemical properties of the surface. The characteristics of activated carbons are determined from nitrogen and benzene isotherms and potentiometric titration data. The properties of pore structure—BET specific surface area, the total pore volume, the external surface area, the micropore volume, and the density of surface charge—are evaluated. The isotherms of benzoic acid adsorption from the aqueous phase are measured for a wide range of solution pH and constant ionic strength by using the static method. The liquid adsorption data are analyzed in terms of the theory of adsorption on heterogeneous solids.

Introduction

The process of adsorption of dissociating organic substances from dilute aqueous solutions at the surface of carbonaceous material is determined by adsorbate, solvent, and adsorbent properties. Adsorbate chemical nature, solubility, its molecular size and shape, type of functional groups, dissociation, association, and solvatation effects are the main factors influencing its behavior. The porous structure, adsorption capacity, and chemical character of surface groups characterize adsorption properties of a solid surface. The presence of other competing solutes and solvent molecules as well as the ionic strength and pH of the solution which determine the solid surface charge may affect the adsorption dramatically. The complexity of adsorption process from a liquid phase makes its theoretical description very complicated.1–7 However, its practical importance, i.e., in environmental protection, wastewater treatment, or some other technological processes, increases the interest in this phenomenon. In many theoretical descriptions the effect of various factors on liquid adsorption was investigated separately. On the other hand, these effects may mutually compensate themselves. Thus, it is very difficult to evaluate exactly the influence of heterogeneity, lateral, or electrostatic interactions separately. It seems to be reasonable to estimate rather the global nonideality of the adsorption system.8,9

Activated carbons are materials of various porous structures and energetic and chemical nonhomogeneity. Their structural heterogeneity is a result of the existence of micro-, meso-, and macropores of different sizes and shapes. The variety of surface groups, impurities, and irregularities determine the energetic heterogeneity and surface charge. In the current work the adsorption properties of activated carbons were studied on the basis of low-temperature nitrogen and benzene isotherms measured over the wide pressure range. The resulting adsorption isotherms were used to evaluate the standard quantities characterizing the surface and structural features of studied carbons: BET specific surface area, the total and micropore volumes, and the mesopore surface area. The electrochemical character and surface charge of their surfaces were determined by potentiometric titration.

The data of benzoic acid adsorption from dilute aqueous solutions on three different activated carbons were described by applying the model of physical adsorption and taking into account an energetic heterogeneity and electrostatic charge of carbon surfaces. The adsorption isotherms were measured at constant ionic strength for a wide pH and concentration range. The theoretical isotherms were fitted to the experimental data by using the optimization method.

Experimental Section

Materials. The experimental granular activated carbons RIAA, RIB, and RIC from Norit n.v. (Amersfoort, The Netherlands) were used as adsorbents. The carbons were washed in a Soxhlet apparatus with HCl solutions of increasing concentrations in order to remove the inorganic impurities. Then, the samples were rinsed with bidistilled water (conductivity 1 μS). The final conductivity of water used for extraction was close to 10 μS. Then, the carbons were dried at 393 K to attain a constant mass.

The adsorbate was benzoic acid of commercially available quality (Merck, Darmstadt, Germany). The liquid mixtures were prepared with bidistilled water.

Methods. Gas Adsorption Experiments. Nitrogen adsorption/desorption isotherms at 77 K were determined volumetrically using an ASAP 2405N analyzer (Micromeritics Corp., Norcross, GA). Benzene vapor adsorption/desorption isotherms were measured at 293 K by a gravimetric method using a McBain-Bakr balance. Potentiometric Titration. Potentiometric titration measurements were performed with a 665 Dosimat (Metrohm, Herisau, Switzerland) combined with a pHm85 Precision pH-meter (Radiometer, Copenhagen, Denmark). The known amount of

* To whom correspondence should be addressed. Fax: (48-81)-5333348. E-mail: annad@hermes.umcs.lublin.pl.
carbon (1 g) was contacted with 50 cm³ of NaCl of ionic strength 0.1 mol dm⁻³ in a special gas-tight vessel thermostated at 293 K and equilibrated for several hours. After each titration step, the drift of the pH value was measured continuously, and the next step was performed only after the drift was smaller than 0.001–0.0001 pH/min. The titration curves were transformed into the surface charge density curves determined from the equation

\[ q_s = F \Delta n / S_{\text{BET}} \]  

(1)

Liquid Adsorption Experiments. The experimental isotherms were measured for benzoic acid adsorbed from dilute aqueous solutions on activated carbons at 293 K at controlled pH and ionic strength (I = 0.1 mol dm⁻³) by using a static method. The pH and ionic strength were adjusted by adding HCl or NaOH and NaCl solutions, respectively. The known amount of activated carbon was first contacted with 5 cm³ of water and degassed under vacuum in Erlenmeyer flasks, and then the adsorbate solution of known concentration was added. The vessels were thermostated at 293 K and agitated until the equilibrium was attained. Finally, the equilibrium solute concentrations were measured by using the UV–vis spectrophotometer Specord M 40 (Carl Zeiss, Jena). The equilibrium pH was also measured for all samples. The adsorbed amount of benzoic acid was calculated from a material balance. For planning the liquid adsorption experiments, the special simulation procedure was used.10

Analysis of Adsorption Data

Carbon Characteristics from Gas Adsorption. Standard Characterization from Nitrogen Data. Nitrogen adsorption data were used to evaluate the BET specific surface area, \( S_{\text{BET}} \), and the total pore volume, \( V_0 \), by applying the standard methods (\( S_{\text{BET}} \) from the linear BET plots and \( V_0 \) from the adsorption at the relative pressure \( p/p_0 = 0.975 \)).11 The external (mesopore) surface area, \( S_{\text{ext}} \), and the micropore volume, \( V_{\text{mic}} \), were obtained from the \( \alpha_r \) plot method.11,12 This method is based on the comparison of a nitrogen isotherm on a studied solid with the standard isotherm on a reference nonporous adsorbent.13 This standard reduced isotherm \( \alpha_r \) is defined as the ratio of the adsorption value corresponding to a given relative pressure \( p/p_0 \) and the adsorption value at the point \( p/p_0 = 0.4 \) (\( p_0 \) is the saturation pressure, and \( p_0 = 0.4 \) is the starting point of the isotherm hysteresis loop for nitrogen adsorption). The micropore structure was characterized by using the distribution function of the mesopore volume relative to the total pore volume \( \Delta V/V \Delta \log(D) = \log(D) \) (\( \Delta V \) is the change of pore volume with the change of pore diameter equal to \( \Delta \log(D) \)). The calculations were performed by applying the de Boer–Jura–Harkins (B–J–H) method.14

Pore Structure from Benzene Adsorption. The mesopore surface area, the micropore volume, and the adsorption capacity were calculated by applying the \( \alpha_r \) plot method. As the standard isotherm, the benzene isotherm on the graphitized carbon black was used.15 In this case the standard reduced isotherm \( \alpha_r \) was defined with respect to the point \( p/p_0 = 0.1754 \) (\( p_0 = 0.175 \) is the starting point of the isotherm hysteresis loop for benzene adsorption).

Adsorption from a Dilute Solution of the Organic Solute. To analyze the data of adsorption from aqueous solutions of benzoic acid, the model of physical adsorption on energetically heterogeneous surfaces was chosen. The benzoic acid can dissociate in aqueous solution over a certain range of pH. During the adsorption process the neutral or ionic forms of solute compete to the adsorbent surface with water molecules; we assume that the other substances used for regulation of solution ionic strength and pH do not participate in this competition. The factors determining adsorption equilibria are as follows: energetic and structural heterogeneities, surface charge determined by solution pH and ionic strength, electrostatic interactions among surface charge and adsorbed molecules, and specific and nonspecific interactions in adsorbed phase.

In terms of the theory of adsorption on energetically heterogeneous solids, the global isotherm equation for such a system may be written in the following way:7

\[ \theta_i = \frac{a_i}{a_m} = \int_{\Delta \theta} \theta_i'(E) \, dE = \int_{\Delta \theta} (\theta_s + \theta_i) \frac{(E_j - E)}{E_j} \, dE_j \]  

(2)

where \( \theta_i \) is the relative adsorption of an organic substance in the adsorption phase, \( a_i \) is the adsorption of an organic solute, \( a_m \) is the maximum adsorption, \( \theta_s \) is the local adsorption on a given surface site, \( \theta_i \) and \( \theta_s \) are the local coverages for neutral (s) and ionic (i) forms of the organic solute. \( E = e/RT \) is the reduced adsorption energy, \( R \) and \( T \) are the ideal gas constant and temperature, and \( \Delta \theta \) is the integration range. The local isotherm has the following form:10

\[ \theta_i = \theta_s + \theta_i = \theta_s [g(c, \rho, pH, E_s) + g(c, \rho, pH, E_j)] = \frac{g_s(c, \rho, pH, E_s) + g(c, \rho, pH, E_j)}{1 + g(c, \rho, pH, E_s) + g(c, \rho, pH, E_j)} \]  

(3)

where \( g(c, \rho, pH, E) \) is the function depending on the adsorption model assumed for neutral (s) and ionic (j) forms of the organic substance and \( c \) is the solute concentration (i = s, j).

For a neutral solute:

\[ g_s(c, \rho, pH, E_s) = g_s(c, \rho, E_s) = K_s c_s \]  

(4)

where \( K_s \) is the equilibrium constant connected with adsorption energy:

\[ K_s = K_{0s} \exp(E_s) \]  

(5)

\( K_{0s} \) is the preexponential factor.

For an ionized solute the effect of electrostatic interactions is taken into account on the basis of electrostatic theory based on the classical Gouy–Chapman model of an electrical double layer:16

\[ g_j(c, \rho, pH, E_j) = K_j g_q \]  

(6)

where

\[ K_j = K_{0j} \exp(E_j) \]  

(7)

In the above, \( K_j \) is the constant describing adsorption of an ionic form, \( q_s \) is the factor determining the effect of surface charge on adsorption, \( z_j \) is the expression determining work necessary to overcome the electrical potential barrier between the solution and solid surface.

F is the Faraday constant, \( z_i \) is the charge of organic ion, and \( \phi_0 \) is the electric interfacial potential.

The value \( \phi(q_i, I) \) is determined from the equation relating it to the charge density of diffuse double layer, \( q_i \), and from the charge balance resulting from system electroneutrality:

\[
q_i(pH, I) + q_s(c_s, pH, I) + q_s(\phi_s) = 0
\]

where \( q_s \) is the density of adsorbed ion charge, \( q_i \) is the density of surface charge determined from the experimental data of potentiometric titration, \( z_i = |z_i| = |z_j| \) is the valence of ions in the diffuse layer, \( e \) and \( l \) are the solution dielectric permittivity and ionic strength.

To simplify the form of integral equation (2), we can assume that the adsorption energies of both solution components are correlated in such a way that their changes show the same tendency—they increase or diminish simultaneously. However, the values of energy changes are not necessarily equal. Thus, one can write:

\[
E_s = E_s(E_i) \quad E_j = E_j(E_s)
\]

In such a case the following relation between the distribution functions for both solute forms exists for a given adsorption site (*):

\[
\int_{E_{s,mn}}^{E_s} \chi(E_s) \, dE_s = \int_{E_{j,mn}}^{E_j} \chi(E_j) \, dE_j = f(E_s^*) = f(E_j^*) = f
\]

In the above, \( f \) is the integral distribution function:

\[
df = \chi(E_i)
\]

Introducing the assumptions (10) and (11) into the integral equation (2), one can obtain the simple form of the isotherm equation for dissociating organic solutes:

\[
\theta_i = \theta_s[g(c_s, pH, E_s) + g(c_i, pH, E_j)] = \int_0^{E_s^*} \left[ g(c_s, pH, E_s) + g(c_i, pH, E_j) \right] \exp[z_i(f)] \left[ 1 + g(c_s, pH, E_s) + g(c_i, pH, E_j) \right] \exp[z_j(f)] \, df
\]

where \( E_i \) (i = s, j) is the mean adsorption energy:

\[
E_i = \int_0^{E_i} f \, df = \int_0^{E_i} \chi(E_i) \, dE_i
\]

and \( z_i \) is the variable describing the distance of adsorption energy \( E_i \) from the mean energy \( E_i \):

\[
z_i(f) = E_i(f) - E_i \quad i = s, j
\]

The adsorption isotherms measured for aqueous liquid systems were analyzed by using eq 13 with the functions \( g \) expressed by eqs 4 and 6. The interfacial electrical potential was calculated from eqs 8 and 9. The Gauss type of distribution function of adsorption energies was assumed to characterize the energetic heterogeneity of adsorption systems. The adsorption capacity was esti-

\[\text{Table 1. Sorption Characteristics of Activated Carbons} \]

<table>
<thead>
<tr>
<th>Activated Carbon</th>
<th>( S_{BET} ) [m(^2)/g]</th>
<th>( S_{mic} ) [m(^2)/g]</th>
<th>( V_0 ) [cm(^3)/g]</th>
<th>( V_{mes} ) [cm(^3)/g]</th>
<th>( V_{mic} ) [cm(^3)/g]</th>
<th>( d_n ) [mmol/g]</th>
</tr>
</thead>
<tbody>
<tr>
<td>RIAA</td>
<td>1450</td>
<td>43</td>
<td>0.73</td>
<td>0.66</td>
<td>58</td>
<td>0.57</td>
</tr>
<tr>
<td>RIB</td>
<td>1190</td>
<td>70</td>
<td>0.64</td>
<td>0.53</td>
<td>98</td>
<td>0.44</td>
</tr>
<tr>
<td>RIC</td>
<td>975</td>
<td>25</td>
<td>0.50</td>
<td>0.45</td>
<td>43</td>
<td>0.38</td>
</tr>
</tbody>
</table>

Figure 1. \( \alpha_s \) plots for nitrogen adsorption on the activated carbons RIAA, RIB, and RIC at 77 K.

Results and Discussion

Carbon Characteristics from Gas Adsorption.

Nitrogen Isotherms. For the activated carbons RIAA, RIB, and RIC the standard quantities were first evaluated: the BET specific surface area, \( S_{BET} \), and the total pore volume, \( V_t \). These values are summarized in Table 1. The external surface area (\( S_{ext} \)) and the micropore volume (\( V_{mic} \)) were calculated from the \( \alpha_s \) plots, which were shown in Figure 1. Table 1 also contains the values of \( S_{mic} \) and \( V_{mic} \).

Analyzing the values of parameters characterizing nitrogen adsorption on the studied carbons (Table 1), one can state that the values of the BET specific surface area, the total pore volume, and the micropore volume are the highest for the carbon RIAA. They decrease for the other two carbons, and they are the lowest for the carbon RIC. However, the activated carbon RIB has a larger external specific area in comparison with those of the other adsorbents. Comparison of the relative values of the micropore volume (\( V_{mic}/V_t \)) and the mesopore surface area (\( S_{mic}/S_{BET} \)) for all carbons shows that they are similar for the carbons RIAA (\( V_{mic}/V_t = 0.90 \) and \( S_{mic}/S_{BET} = 0.03 \)) and RIC (\( V_{mic}/V_t = 0.91 \) and \( S_{mic}/S_{BET} = 0.026 \)) and clearly different for the carbon RIB (\( V_{mic}/V_t = 0.83 \) and \( S_{mic}/S_{BET} = 0.059 \)). This means that the carbon RIAA and especially RIC have a rather uniform microporous structure, whereas in the case of Norit RIB the biporous structure was found.

Figure 2 presents the distribution functions of the relative mesopore volume calculated for nitrogen adsorption isotherms by using the BJH method. For all carbons the main peak is located at the same pore diameter; however, the carbon RIB contains more mesopores than the other two adsorbents.

Benzene Isotherms. The adsorbates used to study the adsorption process from dilute solutions were the derivatives of benzene. It was reasonable to estimate the parameters characterizing benzene vapor adsorption on the activated carbons RIAA, RIB, and RIC. In Figure 3 the isotherms of benzene vapor adsorption are presented.


These isotherms are of type IV according to IUPAC classification. In the case of all isotherms, a sharp increase of adsorption is observed for relative pressures lower than 0.175; this range is attributed to the micropore-filling process. Over the range of greater pressures corresponding to multilayer adsorption and capillary condensation in mesopores, the carbons RIAA and RIC have similar shapes; they are shifted because of the differences in their adsorption capacities. However, for the carbon RIB a greater difference in isotherm character is observed for this range of relative pressures. In comparison to the first two carbons having rather flat segments with the hysteresis loop, for the carbon RIB this part is sharper; this confirms greater contents of mesopores. Benzene isotherms were used to calculate the mesopore surface area, the micropore volume, and the adsorption capacity by applying the $R_s$ plot method. The $R_s$ plots for benzene adsorption are shown in Figure 4. In Table 1 the values of mesopore surface area ($S_{mes}$), micropore volume ($V_{mic}$), and the adsorption capacity ($a_m$) are also presented. Comparing the values of micropore volumes estimated from benzene and nitrogen adsorption, one can state that these values are greater in the case of nitrogen adsorption. This is a result of the smaller sizes of nitrogen molecules, which can penetrate smaller micropores, inaccessible for benzene molecules.

Surface Charge of Activated Carbons. To study the differences in the electrochemical properties of activated carbons, the potentiometric titration experiments were carried out. Figure 5 shows the results of surface charge measurements. Analyzing the presented $q_s = f(pH)$ curves, one can find that the electrochemical character of surfaces is similar for the carbons RIAA and RIB; some differences are observed for lower pH values; both adsorbents have a common point of zero charge ($pH_{pzc} = 7.8$). The carbon RIC has a different chemical character, its zero-charge point is moved toward higher pH values, and it is located at $pH = 9.6$

Adsorption from Dilute Solutions of Benzoic Acid. To analyze the effect of energetic and chemical nonhomogeneity of activated carbons on adsorption from liquid solutions, we measured the isotherms of benzoic acid adsorption from dilute aqueous solutions for the activated carbons RIAA, RIB, and RIC at 293 K. The experimental isotherms are presented in Figures 6–8 in the coordinates $log a$ vs $log c$ for higher (white points) and lower (black points) pH regions. A strong effect of solution acidity on adsorption is observed for all systems. Adsorption of benzoic acid diminishes drastically with an increase of the solution pH. To describe theoretically the studied systems, the model of physical adsorption on energetically heterogeneous solids including the electrostatic interactions between the adsorbent surface and adsorbed species was chosen. In the optimization procedure the parameters of eq 13 were estimated. The values of these best-fit parameters characterizing all experimental adsorption systems are presented in Table 2: the equilibrium constant for a neutral solute, $K_n$, the equilibrium constant for an ionized solute, $K_f$, the reduced energy dispersion, $\sigma$. The optimized isotherms (solid lines), calculated for eq 13 by using parameters obtained from the optimization procedure, are compared with experimental data in Figures...
A good agreement between the experimental points and theoretical curves is found for all analyzed systems (see the values of standard deviations SD from Table 2). (It must be noted that variation of experimental pH values results from various start conditions, e.g., mass/volume ratios. In the optimizations, the experimental pH values have been used. However, the optimized lines are calculated for range-average pH values, and thus discrepancies between experimental points and optimized lines shown in Figures 6–9 are somewhat exaggerated.) This means that the proposed model describes quite well the effect of energetic heterogeneity and surface charge on adsorption equilibria in liquid systems. Comparing the values of equilibrium parameters for neutral and ionic solute forms, one can state that in the case of carbon RIC the nonionized molecules are adsorbed stronger than for the other adsorbents. Then, analyzing the values of relations of equilibrium constants $K_h$ and $K_j$, we find that they are comparable to those of carbons RIAA (19) and RIB (12) and considerably smaller than that for carbon RIC (85). Similarly, the dispersions of adsorption energies are alike for carbons RIAA and RIB, whereas for RIC it is different and clearly higher. In Figure 9 the relative adsorption values are compared for all experimental systems. Stronger relative adsorption is found in the case of carbon RIC as well for low solution pH and for higher range. For two other carbons RIAA and RIB the relative adsorption is comparable. In the earlier discussion we stated that the pore structures of carbons RIAA and RIC were similar, and it was different for RIB. Thus, the actually observed differences in adsorption from the liquid phase for carbon RIC should be related mainly to differences in the chemical properties of adsorbent surfaces. However, the complexity of the adsorption process from solutions does not allow one to distinguish the influences of various parameters on equilibrium. We rather observe the global nonideality effect characterizing the whole system.

**Conclusions**

The discussion of adsorption from gas and liquid phases on three different activated carbons was presented. The nitrogen and benzene vapor adsorption isotherms were used to estimate the values of the BET specific surface area, the total pore volume, the micropore volume, and the external surface area. The parameters characterizing...
the porous structure were compared in order to find the similarities and differences among the studied adsorbents. The electrochemical character of carbon surfaces was also investigated experimentally. The analysis of the adsorption process of benzoic acid from dilute aqueous solutions showed strong differences in relative adsorption for studied systems. It was not possible to separate the influence of various effects.