Impact of the interaction with the positive charge in adsorption of benzene and other organic compounds from aqueous solutions on carbons

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Abstract

We present the results of benzene adsorption at the acidic pH level determined on the series of chemically modified activated carbons and at three temperatures. The influence of carbon surface chemical composition on benzene adsorption is discussed. It is shown that the decrease in the pH level from 7 up to 1.5 increases benzene adsorption and the only exception is carbon modified with gaseous ammonia. Basing on the results of current work and those published previously (for phenol, paracetamol, acetanilide and aniline) and using the results of quantum chemistry calculations (DFT, Gaussian 98) we show, that the value of the energy of interaction with unit positive charge is crucial during the analysis of the influence of pH level on adsorption. Obtained results allow to predict the changes in adsorption of aromatics on carbons with the decrease in the pH level.

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1. Introduction

Benzene is one of the most toxic aromatic hydrocarbons and its removal from wastewater and gasoline in different industrial processes is very important for environmental protection. Carbon surface chemical properties are the main factor influencing adsorption process, especially from aqueous solutions, and its mechanism depends on the differences between chemical properties of an adsorbate and solvent [1]. The influence of solution pH level on adsorption phenomena is very significant since it leads to the change of the effective charge on the carbon surface as well as it can change the degree of the ionization of an adsorbent [2]. In recently published paper [3] we presented a complex study on benzene adsorption from gaseous phase and from diluted aqueous solutions at pH 7 on modified chemically commercial activated carbons. The porosity of studied carbons is the same, while the chemical composition and the acid–base properties of surface layers are drastically different. We reported the mechanism of benzene adsorption and pointed out the analogies between adsorption from gaseous phase and from aqueous solutions. In the current study we report the results of benzene adsorption from aqueous solutions on the same carbons, but measured at the acidic pH level. Moreover, we compare the obtained results with those reported previously for phenol [4], acetanilide [5], aniline [6] and paracetamol [7]. This makes it possible to check how the decrease in pH level of the solution changes the adsorption process and how far this change depends on carbon surface chemical composition.

2. Experimental

Current studies of benzene adsorption from aqueous solutions were performed at pH 1.5 (by addition of concentrated HCl) and at three temperatures 300, 313 and 323 K. We applied the same procedure as reported previously [3]. The equilibrium benzene concentration was detected applying Jasco V-550 UV–vis spectrophotometer (Japan) at the wavelength 254 nm. We studied the commercial D43/1-carbons: initial (D43/1-pure), modified with conc. nitric acid (D43/1-HNO₃), with fuming

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sulphuric acid (D43/1-H$_2$SO$_4$) and with gaseous ammonia (D43/1-NH$_3$). They were characterized by us previously [6]. We showed that they have the same porosity, but drastically different surface chemical composition.

3. Results and discussion

3.1. The calculation of the energy of interaction with the unit positive charge

In the current study all calculations (at B3LYP levels of theory using 6–31 G(d,p) basis sets) were performed using the geometries optimized for the parent compounds. The calculations were performed using Gaussian 98 program [8]. The molecular electrostatic potential (MEP) was calculated at defined points in the range of 1–10 Å from basic site. MEP was calculated along the line parallel to C–N bond for paracetamol (pa), acetanilide (ac) and aniline cation (an$^+$), and C–O bond for phenol (ph) (see Fig. 1). In the case of benzene we choose the line perpendicular to the hexagonal ring above the C atom. The molecular electrostatic potential represents the interaction energy of the system with a unit positive charge. The MEP has been known for a long time [9] to be a reliable descriptor of the hydrogen bond strength: the deeper the electrostatic potential, the stronger the electrostatic interaction with water molecules, H$_3$O$^+$ cation and with hydrogen bond donors in general [10,11]. Moreover MEP has been found to be very useful in understanding sites of protonation on molecules and here we

![Fig. 1. MEP profiles of (A) paracetamol (pa), (B) acetanilide (ac), (C) phenol (ph), (D) benzene (bn) and (E) aniline cation (an$^+$), along the arrow. Note that $R = 0$ is the center of the ring for (A)–(C) and (E) and carbon atom in the case of benzene (D). The pink balls show the position of the positive unit charge in the minimum of the MEP.](image)
inquire whether they can be equally useful in rationalizing H-bond energies between the adsorbed molecule and adsorption site.

The resulting MEP profiles calculated at B3LYP/6-31G(d,p) level are illustrated in Fig. 1. As one can see the energy smoothly and monotonically decreases as the distance (R) decreases confirming that (i) oxygen atoms in pa, ac and ph, and carbon atom in bn are the basic centers and (ii) MEP shows barrierless trajectory, at least at the present level of theory.

The deepest minimum in MEP is observed for pa (−0.228 Hartree). The value of minimum increases in the order of pa < ac < bn < ph it states in good agreement with the increasing acidity of the compounds.

Aniline is known to create cationic form in the acidic solution it is not surprising that in this case MEP is positive in the whole scanned range (Fig. 1E). It is connected to the strong positive charge concentrated on –NH$_3$ group. Here, in correlations shown below, we applied the value of energy of interaction determined at the minimum for aniline molecule.

3.2. Benzene adsorption at the acidic pH level— influence of temperature and carbon surface chemical composition

Fig. 2 shows the adsorption isotherms determined at the acidic pH level and the comparison with those measured at the pH 7. For three carbons, namely initial (D43/1-pure), modified with fuming sulphuric acid and with nitric acid (D43/1-H$_2$SO$_4$; D43/1-HNO$_3$) the rise in adsorption at acidic pH level is observed, and adsorption increases with the temperature. The larger rise in adsorption is observed for acidic carbons, the smallest for the initial one (i.e. amphoteric). Different situation is observed for carbon having strongly basic character i.e. modified with gaseous ammonia (D43/1-NH$_3$). Here the decrease in pH of solution decreases adsorption. Moreover in the range 298–313 K adsorption increases, while at the highest temperature the adsorption drop is seen. The comparison of carbon adsorption capacity for benzene at the acidic pH level leads to the conclusion that unmodified carbon is the best adsorbent, while after modification with acids adsorption decreases. The smaller adsorption is observed for
carbon modified with ammonia, especially in the range of relative concentrations up to ca. 0.2.

Summing up, generally carbon surface modification has the negative influence on benzene adsorption at the acidic pH level comparing to the unmodified carbon, but lowering pH level increases adsorption especially for acid-modified adsorbents, comparing to the neutral pH level.

3.3. Adsorption of organics at the acidic pH level—the role of interactions with the positive charge

Fig. 3 shows the typical correlations obtained for the differences between adsorption at the acidic and neutral pH levels for all studied three temperatures and arbitrarily chosen carbon samples. Those differences were determined from adsorption isotherms at the relative concentrations 0.06 (this value was chosen since aniline adsorption isotherms were determined only up to 0.06 $c_0$ [6]). We include here also the results determined previously for phenol, paracetamol, acetanilide and aniline. Since aniline cation has the positive $E_{\text{MEP}}$ the repulsion with surface protons enables aniline adsorption at the acidic pH level as we shown before [6]. As one can see the remarkable increase in adsorption at the acidic pH level for initial and modified with acids carbons is observed for adsorbates having the $E_{\text{MEP}}/V_{\text{mol}}$ larger that ca. –0.0015 (Hartree mole cm$^{-3}$). Only for carbon modified with ammonia even larger energy is necessary, since only for acetanilide molecule the rise in adsorption at the acidic pH level is observed. This can be explained as follows. For all studied adsorbents at the acidic pH level the additional energy of interaction of adsorbed molecules with surface acidic groups appears. Therefore, those molecules can win the competition with water and interact with surface acidic groups (water is displaced). For ammonia modified carbon this situation is different. As we postulated before, basing on the XPS and resistance measurements, this carbon has pyrrolic nitrogen atoms inside the walls of pores. Those strongly basic nitrogen heteroatoms prefer the interactions with protons and the blocking of pore spaces occurs. This is probably the reason why this carbon behaves in a different way than other adsorbents studied.

4. Conclusions

The decrease in the pH level leads to the rise in benzene adsorption for unmodified carbons and for carbons modified with acids. This is caused by the appearance of the additional energy of interactions between adsorbed molecules and surface acidic groups. The modification with ammonia decreases benzene adsorption, by the blocking of pores by (probably hydrated) basic sites–protons complexes. Using the results of quantum chemistry calculations we show, that the value of the energy of interaction with unit positive charge is crucial during the analysis of the influence of pH level on adsorption. Obtained results allow to predict the changes in adsorption of aromatics on carbons with the decrease in the pH level.

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