АДСОРБЦИЯ 2-ХЛОР-4-НИТРОАНИЛИНА НА АКТИВНОМ УГЛЕ ИЗ РАСТВОРОВ 2-ПРОПАНОЛА

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Изучение закономерностей адсорбции нитросоединений из водных и органических растворителей на поверхности гетерогенных катализаторов позволяет раскрывать особенности интимного механизма их каталитического гидрирования и влияния растворителя на процесс гидрогенизации. В настоящей работе изучена адсорбция 2-хлор-4-нитроанилина на активном угле марки АР-Д из растворов 2-пропанола при температурах 293 и 313 К. Получены изотермы адсорбции, двумерные диаграммы состояния поверхностных слоев и рассчитаны изостерические теплоты процесса. Установлено, что ни модель Лэнгмюра, ни модель БЭТ изотермы адсорбции 2-хлор-4-нитроанилина во всем интервале концентраций корректно не описывают. Наиболее высокую степень линеаризации обнаружил уравнение теории объемного заполнения для мезопористых адсорбентов. Величины теплот являются экзотермическими, и с ростом адсорбции их численные значения по абсолютной величине уменьшаются. Полученные зависимости теплот от количества адсорбированного вещества имеют вид, характерный для адсорбентов с энергетически неоднородной поверхностью. По абсолютной величине теплоны имеют невысокие значения, что позволяет отнести изученный процесс к физической адсорбции. На двумерных диаграммах состояния поверхностных слоев зафиксировано наличие изломов, свидетельствующих об изменениях состояния поверхностных слоев с ростом степени заполнения поверхности углем адсорбатом. Адсорбция 2-хлор-4-нитроанилина на активном угле сопровождается частичной десольватацией компонентов адсорбционного раствора, что, в свою очередь, будет определять знак теплового эффекта и численные значения теплот адсорбции. Кроме того, изменение состояния поверхностного слоя в ходе процесса протекает с "концентрированием" адсорбционного раствора в объеме пор адсорбента.

Ключевые слова: уголь активный, адсорбция, изотермы, диаграммы состояния, поверхностные слои

2-CHLORO-4-NITROANILINE ADSORPTION ON ACTIVE CARBON FROM 2-PROPAHOL SOLUTIONS

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Aromatic nitro compounds, such as nitro anilines and its halogen derivatives, are widely used in the industrial synthesis of dispersed azo dyes and some pharmaceutical products. For its preparation the processes of heterogeneous catalysis in various liquid media are used. One of the most important stages of catalysis, which in some cases determines its rate, is adsorption. The study of the nitro compounds adsorption from aqueous and non-aqueous solvents on the heterogeneous catalysts surface makes it possible to reveal the catalytic hydrogenation intimate mechanism features and the solvent influence on the hydrogenation process. In this work, we studied the 2-chloro-
4-nitroaniline adsorption on active carbon from 2-propanol solutions at 293 and 313 K. Adsorption isotherms, two-dimensional state diagrams of the surface layers were obtained, and the isosteric heats of the process were calculated. The experimental adsorption isotherms are described in the framework of the volume filling of micropores for mesoporous adsorbents theory. The heat of adsorption is negative and decreases in absolute value with increasing degree of surface filling. On two-dimensional surface layers state diagrams the breaks presence, which corresponds to two-dimensional phase transitions, similar to second-order transitions in surface films. This fact indicates changes in the surface layers state with an increase in the degree of filling the coal surface with adsorbate, is observed.

**Key words:** active coal, adsorption, isotherms, state diagrams, surface layers

**INTRODUCTION**

Adsorption phenomena are widespread; therefore, they are of great theoretical and practical interest [1-4]. The issue of surface layer properties during adsorption on solid surfaces is of fundamental importance for fundamental research of surface phenomena and adsorption, and for the development of modern high technologies in the field of hydrogen energy, nanotechnology, petrochemistry and biotechnology.

One of the key areas of adsorption practical application is heterogeneous catalysis. The solution of many problems of both theoretical and applied nature in this area is impossible without taking into account the laws of adsorption of participants in a heterogeneous catalytic process [4, 5], establishing the structure of the adsorption layer and the nature of the interaction of adsorbed substances and the adsorbent. For example, the results of a study of the laws of adsorption of aromatic nitro compounds of various structures complement the array of input data for solving problems of the synthesis and modification of dyes, optical brighteners, pharmaceuticals and substances, the production of components in the production of polymer fibers with unique properties of additives to motor fuels and etc.

The 2-chloro-1,4-phenylenediamine is one of the key compounds used in the production technologies of polymer fibers with enhanced strength properties [6-8], the chemical technology of which is based on the 2-chloro-4-nitroaniline (2C4NA) heterogeneous-catalytic reduction reaction. At the same time, one of the most widely used of organic solvents is 2-propanol. Thus, in its environment, the substrate conversion highest degree is often realized, in addition, it is characterized by wide availability, low cost, and low toxicity [9]. Active carbons have increased mechanical strength and resistance to abrasion, as a result of which they have found primary use as carriers of highly dispersed catalysts.

The purpose of this work was to establish patterns of 2C4NA adsorption on the active carbon AR-D from 2-propanol. To solve the problem posed, it was necessary to obtain experimentally the 2C4NA adsorption isotherms on the active angle at different temperatures, as well as two-dimensional surface layers state diagrams on the angle.

**EXPERIMENTAL PART**

We used 2-chloro-4-nitroaniline brand «chemically pure». It was further purified by double recrystallization from 2-propanol. The adsorbent used was AR-D active carbon with a specific surface area of $755\pm37 \text{ m}^2/\text{g}$, a pore volume of $0.42\pm0.01 \text{ cm}^3/\text{g}$ [10]. The solvent was 2-propanol brand «chemically pure». The 2C4NA adsorption was studied by the volumetric method. Working solutions of a fixed volume and a portion of the active carbon were placed in a hermetic reactor with an isothermal shell. It was maintained at a constant temperature for 40-50 min with occasional stirring. The results of individual experiments have shown that such a time interval is sufficient to establish the adsorption equilibriums in the system. Then samples were taken from the equilibrium mixture. Each aliquot was filtered from coal and diluted several times with 2-propanol to determine the composition of the equilibrium solution.

The 2C4NA equilibrium concentrations were determined by a photometric method on a LEKI SS2110UV spectrophotometer in a quantitative mode of measuring the optical density of the solution. The working wavelength was set separately according to the absorption spectrum of the 2C4NA solutions in 2-
propanol in the concentration range $10^{-2}$-$10^{-5}$ mol/l. Its value was 362 nm, since it was established that, at this wavelength, electromagnetic radiation absorbs only 2C4NA. Errors in the determination of concentrations did not exceed 3-5% of the measured value.

The 2C4NA excess adsorption values were calculated by the ratio:

$$
\Gamma = \frac{(C_0 - C_e)}{m} \cdot V,
$$

In (1): $C_0$ is initial 2C4NA concentration, mol/liter; $C_e$ is equilibrium 2C4NA concentration in the sample, mol/liter; $V$ is the solution volume, liter; $m$ – weight of adsorbent, g.

The structural characteristics of AR-D coal, established by the authors [10], allow us to accept the adsorption volume for the system under study equal to the pore volume of the adsorbent. In this case, the excess adsorption values are equal to the complete adsorption values with an error not exceeding the error of determining the adsorption magnitude. The 2C4NA adsorption isotherms on coal in 2-propanol at temperatures of 293 and 313 K are presented in Fig. 1.

The differential heat of 2C4NA adsorption was determined by the ratio:

$$
\Delta H^\circ = \frac{RT_2 \ln \left( \frac{C_1}{C_2} \right)}{T_2 - T_1},
$$

In (2): $C_1$ and $C_2$ are 2C4NA equilibrium concentrations values in the solution at temperatures $T_1$ and $T_2$, respectively.

The state and structure of surface layers formed on solid surfaces in adsorption are characterized by two-dimensional state diagrams [11-13]. These represent the dependence of two-dimensional surface pressure on the surface area on which accounts 1 mole of adsorbate. The state of the adsorbate in the adsorption volume will be similar to the state of the substance in the surface film. Therefore, the use of two-dimensional state diagrams is an effective way to study the structure of surface layers and adsorption mechanisms.

The two-dimensional surface pressure calculation is based on the estimate of the Gibbs integral [13]:
In equation (3): $\pi$ is the two-dimensional surface pressure, $R$ is the universal gas constant, $\Gamma$ is the excess adsorption, and $C$ is the equilibrium adsorbate concentration.

It was carried out by numerical integration of the experimental adsorption isotherm. The trapezoid method with a large number of integrable dependence points was used as a numerical method. The applying of a large number of points provided the requirement of low error when performing numerical integration. The required number of points of the integrable function was obtained by interpolating the cubic spline function.

The molar area $S_m$ was determined by the equation

$$S_m = \frac{1}{a}.$$  

In equation (4): $a$ – total adsorption value, which is corresponds to the concentration $C$ in equation (3).

As a result of the calculations carried out, two-dimensional state diagrams of the active carbon surface layers were obtained during the 2C4NA adsorption at different temperatures. They are shown in Fig. 4.

On the dependences Fig. 4, arrows indicate fractures that characterize changes in the surface layer state, similar to two-dimensional phase transitions in surface films.

![Fig. 4. State diagrams of the activated carbon AR-D surface layers during 2C4NA adsorption from 2-propanol at temperatures of 293 K (1) and 313 K (2)](image)

RESULTS AND DISCUSSION

The obtained 2C4NA adsorption isotherms on activated carbon in 2-propanol at temperatures of 293 and 313 K (Fig. 1) have the form corresponding to the S-type isotherms according to Giles classification [11]. It was established that the highest degree of the experimental data linearization is achieved by using the MVFT linear coordinates of the equation for mesoporous adsorbents (Fig. 2). In addition, it should be noted that in the concentration range up to $(5.5-7.8) \times 10^{-5}$ mol/l (hereinafter referred to as the region of low concentrations) the adsorption of the organic compound proceeds according to the volume filling mechanism. In the region of concentrations greater than $(5.5-7.8) \times 10^{-5}$ mol/l (hereinafter referred to as the region of high concentrations), none of the equations used correctly describe the experimental dependences.

The resulting heat values are exothermic. With an increase in the adsorption magnitudes, the numerical value of heats decreases in absolute dimension. The dependence of 2C4NA adsorption heat on the values of adsorption (Fig. 3) has the form characteristic of adsorbsents with an energetically inhomogeneous surface [14-16]. The heat absolute dimension has low values. This allows us to relate the studied process to physical adsorption. The adsorption solutions interaction with the surface of the active carbon pores is similar to the liquefaction of vapors of substances in the pores of solids. This is observed when the adsorbate from the gas phase, entering the porous space of the adsorbent, condenses as a liquid. Based on this, it can be assumed that a change in the surface layer state during 2C4NA adsorption on the active carbon is accompanied by a «concentration» of the adsorption solution in the adsorbent pore volume. Physically justified such a process can be described as the removal of a solvent part from the adsorption solution volume into the bulk phase.

On two-dimensional state diagrams (Fig. 4), with the values of the molar area corresponding to the boundary of the areas of low and high concentrations, there is a break (marked by an arrow). On the surface films state diagrams $\pi = f(S_m)$ such changes are explained by a two-dimensional phase transition, for example, a transition from a «gas» film to a «liquid» film. In the case of the active carbon state diagram in 2C4NA adsorption from 2-propanol solutions, such a fracture suggests that 2C4NA state in the adsorption volume of active carbon changes with varying nitro compound concentration in the solution. This transition is attributed to the adsorption values of $(2.7-7.1) \times 10^{-5}$ mol/g. In addition, a change in the state of the surface layer may be accompanied by partial desolvation of the adsorption system components, which, in turn, will determine the sign and magnitude of the heats of adsorption.

The liquid-phase systems studies [17-20] have shown that the solvent has a significant role in processes involving liquid media. That is why, it should be concluded that to accurately determine the nature and patterns of the solvent effect on the organic compound adsorption by the adsorbent surface in the 2C4NA–2-propanol–active carbon systems further studies are needed to investigate the adsorption in aqueous and aqueous-organic solvents of different composition.
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