Heats of adsorption of hydrocarbons on solid surfaces

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The integral heats of the interphase interaction of liquid aliphatic and aromatic hydrocarbons with fibers and powders of polyacrylonitrile and polypropylene, clay, and sandstone at 293 and 303 K were evaluated microcalorimetrically. The relationships between the heat of adsorption of hydrocarbons and the sorbate : adsorbent mass ratio were obtained. The heat and time needed for the interaction of hydrocarbons with the solid surfaces to reach equilibrium depend mainly on the adsorbent structure.

Key words: adsorption, heat of adsorption, aliphatic and aromatic hydrocarbons, polyacrylonitrile and polypropylene fibers, powders, clay, sandstone.

Based on the data from the literature for adsorption of polar compounds on the polystyrene and cellulose surfaces, the authors[1] believe that the adsorption of organic substances, as a rule, is exothermic. However, when hydrocarbons are adsorbed by various materials, heat can be consumed. For example, benzene is adsorbed on the carbon fibers and graphitized carbon black with heat release,[2,3] and its interaction with active carbon involves heat absorption.[4] Hexane is adsorbed on the montmorrilonite surface with heat release,[5] while cyclohexane is adsorbed with heat absorption.[6] The heats of adsorption of hydrocarbons measured by the direct calorimetric method and calculated from the adsorption isotherms for the same adsorption systems are different. Works on heats of adsorption of hydrocarbons on the surface of polymeric materials determined by the direct method are lacking, although synthetic polymeric adsorbents are used for purification of water[7] and air[8] from petroleum products. In this work, the heats of interaction of liquid model aliphatic and aromatic hydrocarbons with fibers and powders of polyacrylonitrile and polypropylene, clay, and sandstone at 293—333 K were determined microcalorimetrically, and their relationships to the sorbate : adsorbent (S : Ad) mass ratio were studied.

Experimental

Heats of interaction between liquid hydrocarbons and the surfaces of various materials were determined using an MKDP-2 microcalorimeter.[9] The total heat (Q/J), the heat of adsorption (ΔH/J mol^{-1}), and the intensity of thermal flow (W/J s^{-1}) were calculated using the formulas

$$Q = S\alpha,\ \Delta H = Q/n,\ W = h\beta,$$

where S is the surface area under the experimental thermogram/cm^2; α is the calibration coefficient for the determination of the surface area under the detected thermogram, which takes into account the resistance and current strength of the conductor and the sensitivity of the amplifier and recording device/J cm^{-2}; n is the number of moles of the sorbate; h is the height of the thermogram corresponding to a certain time of recording in the stationary regime/mm; β is the calibration coefficient for the determination of the height of the detected thermogram, which takes into account the resistance and current strength of the conductor and the sensitivity of the amplifier and recording device/J s^{-1} mm^{-1}. The sensitivity of the instrument was $5.911 \cdot 10^{-5}$ J s^{-1} mm^{-1}. The heat of each hydrocarbon—adsorbent interacting system at equilibrium was determined as an average of three measurements at constant doses and weighed samples of the adsorbate and adsorbent. Experimental thermograms were processed by the programming method, including numerical integration. The standard deviation of the heat values did not exceed 6—8% in the whole interval. The specific surface of adsorbents was determined from the heats of adsorption using a known method.[10] Liquid aliphatic (*n*-hexane, cyclohexane, *n*-heptane, *n*-octane, isooctane, *n*-nonane, *n*-decane, *n*-undecane, *n*-tetradecane, and *n*-pentadecane) and aromatic (benzene, toluene, and *p*-xylene) hydrocarbons (reagent grade) were used as sorbates (S). They were additionally distilled and stored in sealed vessels over freshly calcined NaA zeolites. Fibers of polyacrylonitrile (PAN) and polypropylene (PP), isotactic polypropylene powder, clay, and sandstone were used as adsorbents (Ad). Samples of synthetic polymers were evacuated before experiment for 2 h at 50—60 °C. The clay and sandstone samples were treated according to the previously described procedure.[11] The particle size of the adsorbent powders was 200—250 μm.

Results and Discussion

General characteristic of adsorption thermograms. The adsorption of aliphatic and aromatic hydrocarbons on the PAN fiber surface occurs rapidly (10—15 min), being an exothermic process (Fig. 1). When the number of carbon

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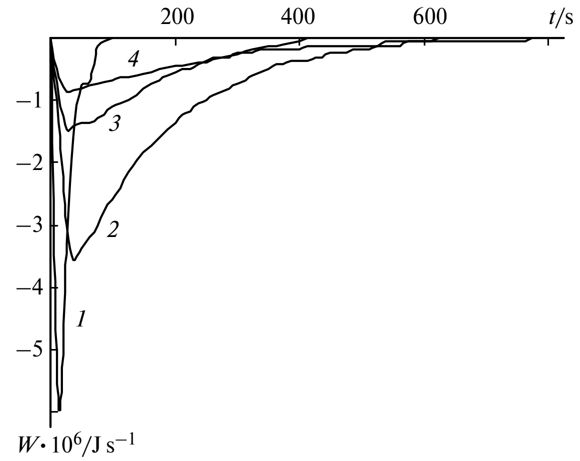

Fig. 1. Thermograms of adsorption of hexane (*1*), decane (*2*), toluene (*3*), and *p*-xylene (*4*) on the PAN fiber at 293 (*1*, *4*) and 303 K (*2*, *3*).

atoms in the molecule of normal aliphatic hydrocarbons (hexane, octane, decane, undecane, and pentadecane) increases, the heat of adsorption ($-\Delta H$) decreases from 120 to 30 J mol^{-1} under the conditions of a sorbate excess (S : Ad = 0.37 : 0.20). The heat of adsorption of aromatic hydrocarbons on the PAN fiber decreases in the series benzene > toluene > *p*-xylene, being 140, 120, and 60 J mol^{-1}, respectively. The interaction of the same aliphatic and aromatic hydrocarbons with the PP fiber is accompanied first by the release and then by the absorption of heat, and compared to PAN fiber the process is characterized by a longer time for the heat equilibration (50 min) (Fig. 2). The adsorption of aliphatic and aromatic hydrocarbons on the PP fiber is accompanied by higher positive heat effects at the S : Ad ratios ≤1 (Fig. 3). Except for benzene, the hydrocarbons interact with the surface of the PP fiber and powder with the high initial heat effects (see Fig. 2). The adsorption of the hydrocarbons on the PP powder occurs with a more intense heat consumption than that on the PP fiber, although the equilibration times for both processes are close.

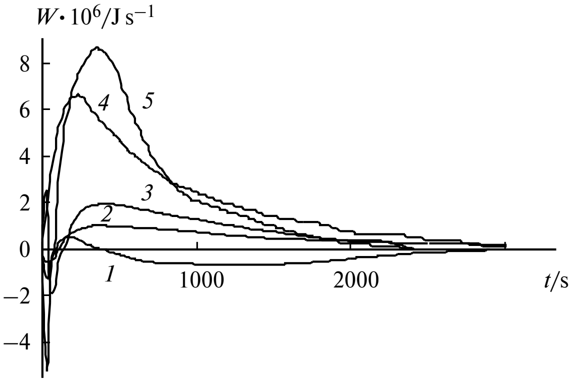

Fig. 2. Thermograms of adsorption of benzene (*1*), hexane (*2*, *5*), toluene (*3*), and decane (*4*) on the PP fiber (*1*, *2*) and PP powder (*3*—*5*) at 293 K.

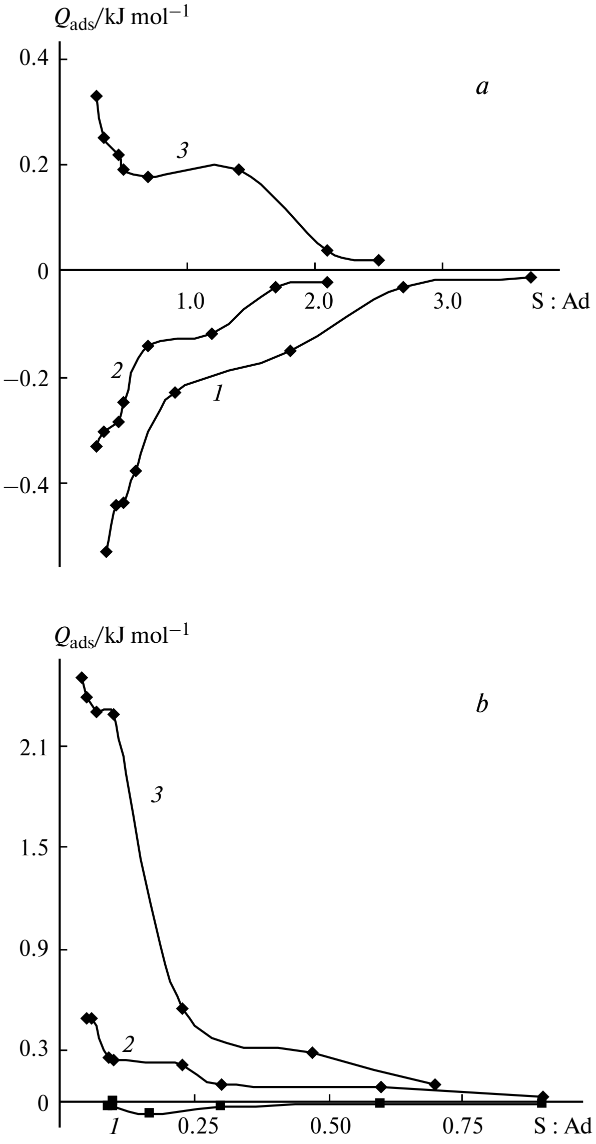

Fig. 3. The heats of adsorption of toluene (*1*), isooctane (*2*), and decane (*3*) on the PP fiber (*a*) and PP powder (*b*) as a function of the S : Ad ratio at 293 K.

The character of adsorption of the hydrocarbons on clay and sandstone does not basically differ from the adsorption on the polymeric materials: the endothermic component of the total heat of the interphase interaction is higher than the exothermic term. For example, a low initial release of heat observed on adsorption of cyclohexane, isooctane, benzene, toluene, and *p*-xylene on clay ($-\Delta H$ = 0.18—0.76 J mol^{-1}) is followed by a considerable heat consumption with increasing loadings (ΔH = 27.0—89.0 J mol^{-1}). The adsorption of normal C_6—C_{14} hydrocarbons on clay is accompanied only by heat absorption, which increases from 170 (hexane) to 2540 J mol^{-1}

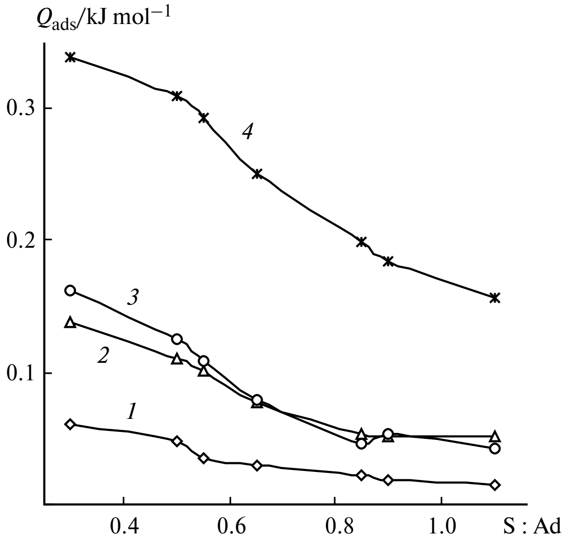

Fig. 4. The heats of adsorption of hexane (*1*), heptane (*2*), isooctane (*3*), and decane (*4*) on clay as a function of the S : Ad ratio at 293 K.

(tetradecane) with the elongation of the carbon chain at the mass ratio S : Ad = 1.1 : 1.0. The interaction of the hydrocarbons with clay can be characterized as a fast process. For the adsorption of the hydrocarbons on sandstone, the interphase interaction is very weak (3—13 J mol^{-1}), and equilibrium is established rather slowly (to 146 min).

Dependence of the heats of adsorption on the sorbate : adsorbent ratio. Analysis of the thermograms (see Figs. 1 and 2) and heats of adsorption (Figs. 3 and 4) shows that the value and sign of the thermal effect along with the time needed to equilibrate adsorption of hydrocarbons on the surfaces depend on the composition and structure of components of the system (hydrocarbon and adsorbent) and the S : Ad ratio.

For example, an increase in the S : Ad mass ratio from 0.1 to 3.7 results in a decrease in the integral heat of the exo- and endothermic interactions of hydrocarbons with the surfaces of fibrous (see Fig. 3, *a*) and powdered (see Fig. 3, *b*) polypropylene, clay (see Fig. 4), and sandstone. On the PP fiber surface (see Fig. 3), the heat effect of adsorption of toluene (curve *1*) and isooctane (curve *2*) is exothermic, although under the same conditions the endothermic effect is observed on the powder surface (see Fig. 3, *b*, curves *2* and *3*). The exothermic thermal effect for toluene adsorption on the PP fiber (see Fig. 3, *a*) is 440 J mol^{-1}, while the adsorption on the PP powder is accompanied by a weak heat release (20 J mol^{-1}) under the same conditions of interaction of the phases (see Fig. 3, *b*, curve *1*). The further process of toluene adsorption occurs with heat consumption until the heat equilibrium is established (curve *3*). The heat of adsorption of aliphatic hydrocarbons on clay in the S : Ad interval studied increases with an increase in the number of carbon atoms in the chain (see Fig. 4). The shape of the ΔH plot *vs.* S : Ad ratio for the adsorption process on sandstone is the same as the plot for adsorption on clay.

Small heats of adsorption of the hydrocarbons on the solid surfaces (from −500 to +2500 J mol^{-1}) are comparable with the heats of interaction of chlorobenzene and benzene with alumina[12] and of alcohols with the cellulose fiber[13] and are characteristic of physical adsorption. However, for the interphase interaction of the hydrocarbons with the polymers and clay (see Figs. 2—4), the sign of the thermal effect changes, and the equilibration time depends on the chemical nature and structures of the sorbate and adsorbent and their ratio.

Analysis of the thermograms (see Figs. 1 and 2) shows that the change in the sign of the thermal effect of hydrocarbon adsorption and the equilibration time depend on the texture of the adsorbent surface rather than on its specific surface, chemical nature, and composition. This corresponds to the dynamic character of physical adsorption. The adsorption of hydrocarbons on the smooth surface of the PAN and PP fibers, whose polymeric chains adopt a certain space orientation, has an appreciable degree of localization with formation of polymolecular layers. Accordingly, the adsorption of hydrocarbons on fibers is accompanied, in most cases, by heat release (see Figs. 1 and 3, *a*). Adsorbed hydrocarbon molecules are bound less strongly to the porous surfaces of the PP powder and clay. For example, the specific surfaces of the PP fiber and powder are close (36 and 49 m^2 g^{-1}),[10] and the heats of adsorption of hydrocarbons on the PP powder and PP fiber differ in sign and value (see Fig. 3). The heat effects of adsorption of, *e.g.*, decane on the PP fiber and clay are approximately the same (see Figs. 3, *a* and 4), and the specific surface of clay (14 m^2 g^{-1})[10] is 3.5 times less than that of the fiber specific surface. These processes are characterized by heat absorption, because the self-diffusion and transfer of the adsorbed molecules to micro- and macropores require high energies (see Figs. 3, *b* and 4). Finally, an additional heat absorption can be caused by the phase transition of hydrocarbons adsorbed in the micropores.[10,14]

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