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Adsorption of chlorobenzene and benzene on γ-Al_2O_3

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Adsorption of chlorobenzene and benzene on γ-Al_2O_3 was investigated in the 413—572 K temperature region at an adsorbate partial pressure ranging from 2 to 1000 Pa. The adsorption isotherms were measured and the isosteric heats and the entropy characteristics of adsorption were determined. The experimentally found and theoretically calculated entropy changes upon adsorption were compared. The mobility of the molecules of both adsorbates in the adsorption layer was limited with respect to that predicted by the ideal two-dimensional gas model. The mechanism of adsorption of benzene and chlorobenzene is discussed.

Key words: adsorption, thermodynamics of adsorption, alumina, chlorobenzene, benzene.

Study of adsorption of chlorobenzene (CB) on γ-Al_2O_3 is important regarding the development of an adsorption-catalytic method for the utilization of CB contained in gas effluents. Previously, adsorption isotherms in the 900—23600 Pa range of partial pressures have been measured.[1] It was of interest to measure the adsorption isotherm of CB on γ-Al_2O_3 for lower partial pressures and to study the thermodynamics of this process.

Some information about the mechanism of adsorption of CB on γ-Al_2O_3 can be gained from comparison of thermodynamic characteristics of the adsorption equilibrium of CB and benzene.

Determination of the heat of adsorption[2,3] and adsorption isotherms[4] of benzene on Al_2O_3 is documented. However, in none of these studies was γ-modification of the oxide used, although the adsorption properties of alumina depend substantially on the crystal form.[5] Therefore in this work, we studied the thermodynamics of adsorption of benzene on γ-Al_2O_3.

Experimental

Alumina was prepared by the scheme bayerite→boehmite→γ-Al_2O_3.[5] To prepare bayerite, a stoichiometric amount of a 14% solution of NH_3 (analytically pure grade) was added with stirring at 303 K to a 0.5 *M* solution of $AlCl_3$ (analytically pure grade) and then the pH of the suspension was brought to 10—11. The mixture was stirred at this temperature for 1 h, filtered, washed on the filter to completely remove Cl^- ions, and dried at 363 K. The xerogel was suspended in distilled water and the pH of the suspension was brought to 11 by adding a concentrated solution of NH_3. After aging for 10 days, the precipitate was filtered off, washed several times on the filter with hot water, and dried at 383 K. The bayerite thus synthesized was treated with a 20% solution of NH_3 in an autoclave for 10 h at 473 K to give boehmite. The precipitate of boehmite was washed on the filter to a neutral pH and dried at 383 K. Calcination of boehmite at 723 K for 5 h gave γ-Al_2O_3. The phase composition of the products was checked at each step of the synthesis by X-ray diffraction powder analysis on a DRON-2 diffractometer. The specific surface area of alumina, determined from low-temperature adsorption of nitrogen, was 160 $m^2\ g^{-1}$ and the content of structural water corresponded to the formula $Al_2O_3 \cdot 0.2H_2O$.

Adsorption isotherms were determined by chromatography[6] on a Tsvet-500 chromatograph with a flame ionization detector. Helium dried by commercial alumina and CaA zeolite was used as the carrier gas. The rate of the carrier gas was 30 mL min^{-1}. The 0.2—0.315 mm fraction of γ-Al_2O_3 was used in the investigations. The stainless-steel column (270×4 mm) was conditioned at 573 K for 6—8 h prior to experiments. The weighed portion of γ-Al_2O_3 in the column was 0.803 g.

Benzene (chemically pure grade) and CB were additionally distilled and stored in tightly closed vessels over freshly calcined NaA zeolite. Adsorbate samples were introduced into the column as a vapor through a heated dispensing cock. The gas—vapor mixture was prepared by saturating helium with the vapor of the compound in a saturator maintained at a constant temperature. The detector was calibrated against neat liquids.

Adsorption isotherms of CB were determined in the temperature range of 463—572 K, those of benzene, in the 413—473 K range. Variation of the carrier gas flow rate from 20 to 40 mL min^{-1} resulted in insignificant changes in the position of the isotherm, *i.e.*, the diffusion and kinetic broadening of the chromatographic peak could be neglected under the experimental conditions.

The relative error of determination of the adsorbate partial pressure (p) and the excessive adsorption (Γ) was ~7% and remained virtually constant over the whole ranges of p and Γ studied. About half of this value is due to systematic errors.

The isosteric heat of adsorption (q_{st}) was calculated from the $\ln p$—$1/T$ plot. The absolute error of the calculation of $\ln p$ was equal to the relative error of determination of p. As noted above, the latter value does not depend on p; therefore, the presence of the systematic error gives straight lines parallel to the actual isotherm and having the same slope. Hence, the systematic errors of determination of the adsorbate partial pressure did not influence the accuracy of calculation of q_{st}. This value was subject only to random errors and, with a confidence

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probability of 0.95, it was equal to ~3 and 4 kJ mol^{-1} for CB and benzene, respectively.

Based on the data on the accuracy of determination of p, Γ, and q_{st} and using the rule for calculation of the inaccuracy for a value determined indirectly,[7] the errors of determination of the differential entropy of an adsorbed substance ($\bar{S}^s$) and the corresponding standard value ($\bar{S}^{s\circ}$) were estimated to be 6.5, and those for the change in the differential entropy upon adsorption ($\Delta\bar{S}^s$) were found to be 6 J mol^{-1} K^{-1}.

Results and Discussion

The resulting adsorption isotherms of benzene and CB (Fig. 1) are well described by the Freundlich adsorption isotherm (FI), $\Gamma = Cp^{1/n}$, where Γ is the excessive adsorption, mol g^{-1}; p is the partial pressure of the adsorbate, Pa; and C and n are constants; the correlation coefficient was $r^2 > 0.998$ in all cases.

As the temperature increases, the coefficient n, characterizing the "degree of non-linearity" of the isotherm, decreases approaching unity. For benzene, the dependence of n on T in the temperature range studied can be described by the function $n(T) = 560/T$ and for CB it corresponds to the equation $n(T) = 0.345 + 394/T$.

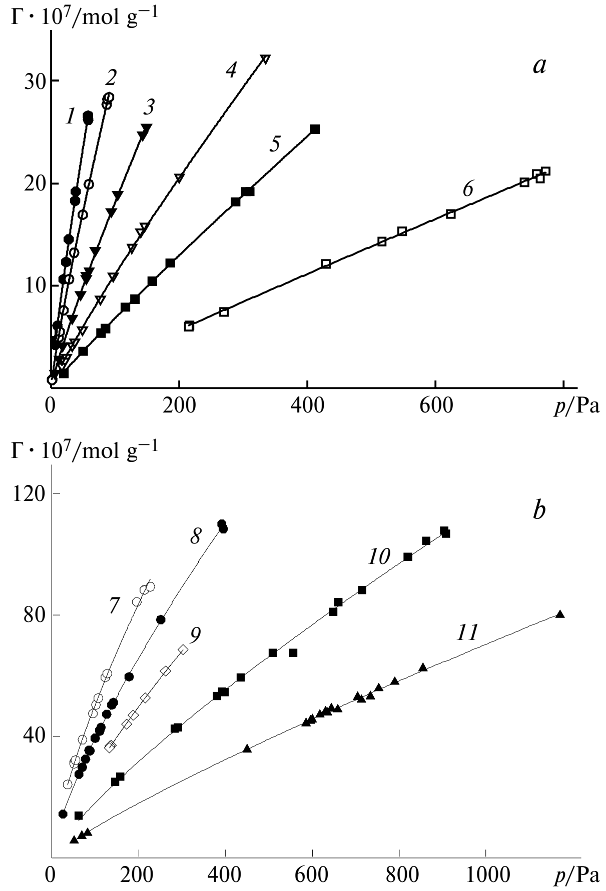

Fig. 1. Adsorption isotherms of chlorobenzene (*a*) at temperatures of 463 (*1*), 473 (*2*), 493 (*3*), 513 (*4*), 533 (*5*), and 572 K (*6*) and benzene (*b*) at 413 (*7*), 423 (*8*), 433 (*9*), 453 (*10*), and 473 K (*11*).

It is known that q_{st} can be determined from the equation

$$(\log p)_\Gamma = -q_{st}/(RT) + \text{const}, \tag{1}$$

which does not take into account the temperature dependence of q_{st}, or from an equation that does take into account this dependence in the first approximation[8]

$$(\ln p)_\Gamma = -\frac{q_{st}(\hat{T}) + \Delta C_p \hat{T}}{RT} - \frac{\Delta C_p}{R}\ln T + \text{const}'. \tag{2}$$

Here $\hat{T}$ is the simple average temperature over the temperature range studied, which is equal to 508 and 439 K for CB and benzene, respectively; $\Delta C_p = C_{p,\text{ads}} - C_{p,\text{g}}$, where $\Delta C_p \neq f(T)$; $C_{p,\text{ads}}$ and $C_{p,\text{g}}$ are the heat capacities of the adsorbate in the adsorbed and gas phases, respectively. The subscript Γ means that this isostere equation refers to a definite Γ value. In addition to q_{st}, Eq. (2) allows one to calculate ΔC_p by means of the Markwardt method.[9]

As shown by statistical analysis, the accuracy of experimental data on the adsorption of CB permits the calculation of q_{st} from Eq. (2); the q_{st} values calculated from Eqs. (1) and (2) differ by no more than 0.5 kJ mol^{-1}, which is much smaller than the error associated with actual regression. It proved impossible to process the data on benzene adsorption using Eq. (2). The dependences of q_{st} on Γ are shown in Fig. 2.

The ΔC_p value for CB averaged over the range of adsorptions studied amounts to 110±60 J mol^{-1} K^{-1}. This value was used to convert the data on CB adsorption obtained for 508 K to 439 K, *i.e.*, to the temperature for which the adsorption characteristics of benzene were measured.

The heat capacity of CB in the adsorbed state is much greater than its heat capacity in the gas phase ($C_{p,\text{g}}(508) = 152.9$ J mol^{-1} K^{-1}).[10] A similar situation was observed for adsorption of various hydrocarbons on Silochrome[11] and pentane on graphitized carbon black (GCB).[12]

Since the number of degrees of freedom of molecules upon adsorption decreases, the increase in the heat

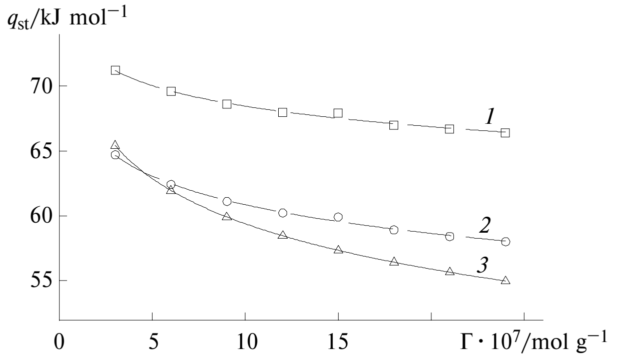

Fig. 2. Isosteric heats of adsorption *vs.* excessive adsorption for chlorobenzene at 439 (*1*) and 508 K (*2*) and benzene at 439 K (*3*).

capacity of a substance in the adsorbed phase with respect to that in the gas phase can be due to the interaction between the adsorbed molecules and the adsorbent surface. This interaction proves to be the channel of the transfer of energy from the adsobate molecule to the portion of the surface in the close vicinity of the site of adsorption. Thus, some part of the surface below the adsorbed species is involved in the energy distribution over degrees of freedom; it is this process that determines the increases the heat capacity $C_{p,\mathrm{ads}}$.

It has been shown[13] that the dependence of q_{st} on Γ for the FI obeys the equation

$$q_{st} = q_0 + RT^2n'(T)\ln\Gamma, \qquad (3)$$

where $n'(T) = \mathrm{d}n'(T)/\mathrm{d}T$, q_0 is a constant. According to regression analysis, the variation of q_{st} with Γ for both compounds is described adequately by a logarithmic equation and the regression pre-logarithmic factor coincides almost exactly with that calculated from Eq. (3) for CB (deviation 1.6%) and differs only slightly in the case of benzene (8%).

The rather great q_{st} values for CB and benzene point to the possibility of chemisorption.

The heats of adsorption of CB are somewhat higher than those for benzene (see Fig. 2), which is in line with a higher polarity of CB (the dipole moment of the CB molecule is 1.7 D). The small difference between the heats may be due to the fact that the introduction of the heteroatom gives rise to two opposite effects. On the one hand, the adsorption interaction is enhanced due to the higher dipole moment of the CB molecule, *i.e.*, to stronger electrostatic interaction with the potential field of the adsorbent surface. In addition, the influence of the proper heteroatom is also possible, for example, this can give rise to the stronger two-center adsorption similar to the adsorption of CB on the hydroxylated surface of rutile, described previously,[14] or the interaction of the Cl atom with the surface aluminum ions. On the other hand, the negative inductive effect of the Cl atom decreases the electron density on the aromatic ring and, hence, makes the hydrogen bond between the surface OH groups and the benzene ring π-electrons weaker than that in the case of benzene. A similar effect has also been found for the hydroxylated surface of rutile[14] and ZnO.[15]

Knowing q_{st}, we can calculate the change in entropy upon adsorption[8]

$$\Delta\bar{S}^s = \bar{S}^s - \tilde{S}_g = -q_{st}/\hat{T},$$

where $\tilde{S}_g$ is the entropy of the adsorbate in the gas phase.* From the known $\tilde{S}_g$, the $\bar{S}^s$ value was found. All the characteristics described above refer to the temperature $\hat{T}$. The $\tilde{S}^\circ_g(\hat{T})$ dependences were calculated from the standard entropies $\tilde{S}_g(298)$ and using the $C_{p,g}(T)$ dependences, available from the literature.[10,16] The value p_0 = 101325 Pa was taken as the standard pressure. The known relation

$$\tilde{S}_g(\hat{T},\Gamma) = \tilde{S}^\circ_g(\hat{T}) - R\ln[p(\hat{T},\Gamma)/p_0],$$

where $p(\hat{T},\Gamma)$ is the equilibrium partial pressure of the adsorbate at the temperature $\hat{T}$ and adsorption Γ, makes it possible to pass from the standard entropy to equilibrium entropy. The calculated values $\Delta\bar{S}^s$ and $\bar{S}^s$ for CB and benzene are listed in Tables 1 and 2. Table 2 also presents the entropy characteristics of CB converted to 439 K.

It has been shown previously[13] that, if the adsorption isotherm is described by the Freundlich equation, the differential entropy can be calculated from the formula

$$\bar{S}^s = \bar{S}^{s\circ}(\hat{T}) - R[n(T) + Tn'(T)]\ln\Gamma. \qquad (4)$$

It was proposed to use this expression as one of the criteria that allow one to find out whether experimental results obey the Freundlich equation. Yet another criterion is the correspondence of the variation of q_{st} *vs.* Γ to Eq. (3). As can be seen from the foregoing, this criterion is fulfilled.

If the dependence of the entropy of the adsorption phase on the amount adsorbed actually does satisfy

Table 1. Entropy characteristics of chlorobenzene adsorption at 508 K for various values of excessive adsorption (Γ)

$\Gamma \cdot 10^7$ /mol g^{-1}	$-\Delta\bar{S}^s$	$-\Delta\bar{S}_{\mathrm{theor}}$	$\bar{S}^s$	$\bar{S}^{s\circ}$
	J mol^{-1} K^{-1}			
3	127.4	97.5	322.7	279.6
6	122.9	96.7	320.7	279.5
9	120.3	96.9	320.1	280.1
12	118.6	95.6	318.1	278.9
15	117.2	96.2	318.2	279.7
18	116.0	95.3	317.0	279.0
21	115.0	95.6	317.0	279.4
24	114.2	96.1	317.2	280.0

Table 2. Entropy characteristics of benzene and chlorobenzene adsorption at 439 K for various values of excessive adsorption (Γ)

$\Gamma \cdot 10^7$ /mol g^{-1}	Benzene			Chlorobenzene		
	$-\Delta\bar{S}^s$	$-\Delta\bar{S}_{\mathrm{theor}}$	$\bar{S}^s$	$-\Delta\bar{S}^s$	$-\Delta\bar{S}_{\mathrm{theor}}$	$\bar{S}^s$
	J mol^{-1} K^{-1}					
3	149.0	100.7	239.6	162.3	116.7	287.8
6	141.1	99.8	240.2	158.5	115.3	284.4
9	136.5	98.2	240.5	156.3	115.1	283.0
12	133.2	97.5	240.8	154.9	113.6	280.5
15	130.6	97.0	240.9	153.7	114.0	280.3
18	128.5	96.6	241.1	152.7	112.9	278.7
21	126.8	96.2	241.3	151.9	113.0	278.3
24	125.2	95.9	241.4	151.2	113.4	278.3
40	119.4	94.8	241.8	—	—	—
80	111.4	93.2	242.4	—	—	—

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* The "bar" and "tilde" signs imply differential and molar average values, respectively.

Eq. (4), the $\bar{S}^{\mathrm{s}\circ}(T)$ value would not vary with Γ. The $\bar{S}^{\mathrm{s}\circ}(\hat{T})$ value for CB is really constant; the deviations are random rather than regular and they are much smaller than the above indicated inaccuracy (see Table 1). In the case of benzene, the pre-logarithmic factor in Eq. (4) becomes equal to zero, and the equality $\bar{S}^{\mathrm{s}} = \bar{S}^{\mathrm{s}\circ}$ is expected to hold. In reality, insignificant monotonic increase in entropy is observed. The change in the $\bar{S}^{\mathrm{s}}$ value over the whole range studied was 2.6 J mol^{-1} K^{-1}, which is within the limits of experimental error. Hence, $\bar{S}^{\mathrm{s}\circ}(\hat{T})$ can formally be assumed to be constant and the average $\bar{S}^{\mathrm{s}}$ value, equal to 241 J mol^{-1} K^{-1}, can be taken for benzene.

Previously, it has been shown[17] that the thermal entropy ($\bar{S}_{\mathrm{therm}}$) of several hydrocarbons adsorbed on a nonpolar homogeneous adsorbent (GTB) coincides with their entropy in the liquid state ($\tilde{S}^{\circ}$(liq)). It is of interest to find out whether this regularity holds for adsorption on alumina, which is a polar nonhomogeneous sorbent.

Proceeding from Eq. (4) and using the above-described method,[18] we can derive the following relation:

$$\bar{S}_{\mathrm{therm}} = \bar{S}^{\mathrm{s}\circ}(\hat{T}) - R[n(\hat{T}) + Tn'(\hat{T})]\ln\Gamma_{\mathrm{m}},$$

where Γ_{m} is the adsorbed amount corresponding to a monolayer coverage. It is fairly difficult to determine unambiguously the Γ_{m} values[19]; therefore, the formal procedure can be used.[17] The molecular area of CB, needed to calculate the monolayer adsorption, has been assumed to be 0.465 nm^2 (see Ref. 15). For benzene, $\bar{S}_{\mathrm{therm}} = \bar{S}^{\mathrm{s}\circ}$; therefore, calculation of Γ_{m} was not required. The $\bar{S}_{\mathrm{therm}}$ value for CB at 508 K is equal to 301 J mol^{-1} K^{-1}, while that for benzene at 439 K is 241 J mol^{-1} K^{-1}. These results coincide with the entropies of CB and benzene in the liquid state at the corresponding temperatures calculated from thermodynamic data[10,16,20] (300 and 232 J mol^{-1} K^{-1}, respectively).

The view on the similarity of properties of substances in the liquid and adsorption phases follows from the Polanyi potential theory,[19] which postulates enhancement of the intermolecular interactions in the field of adsorption forces and compression of the adsorption phase to a liquid-like state.

Yet another interpretation of the fact that the $\bar{S}_{\mathrm{therm}}$ and $\tilde{S}^{\circ}$(liq) coincide can be proposed without resorting to the potential theory. Thermal entropy characterizes the state of the adsorbate in the adsorption phase in which its mobility is limited by the surface and by the potential field of the adsorbent. Since the mobility of a molecule in liquid is restricted by neighboring molecules, the state of a substance in the adsorption field is close to the state of the liquid phase.

Some information concerning the mobility of molecules in the adsorption layer can be gained from comparison of the $\Delta\bar{S}^{\mathrm{s}}$ values calculated theoretically and found experimentally.[21] Let us consider the simplest model of an ideal two-dimensional gas in which one degree of freedom of the forward motion has been lost. We assume that the vibrational and rotational degrees of freedom are retained intact upon adsorption. The decrease in entropy is represented by the relation[21]

$$-\Delta\tilde{S}_{\mathrm{theor}} = R\ln(\Gamma_{\mathrm{s}}/c) + R[0.5 + \ln(2\pi mkT/h^2)^{0.5}],$$

where *c* is the adsorbate concentration in the equilibrium gas phase, *m* is the mass of the adsorbate molecule, *h* is the Planck constant, *k* is the Boltzmann constant, and Γ_{s} is excessive adsorption per unit surface area of the adsorbent.

The $\Delta\tilde{S}_{\mathrm{theor}}$ value is molar average. To pass to the differential value, one should use the equation[13]

$$\bar{S}^{\mathrm{s}} = \tilde{S}^{\mathrm{s}} - R[n(T) + Tn'(T)],$$

which relates the molar average and differential entropies in the case where the adsorption isotherm is described by the Freundlich equation. Then

$$\Delta\bar{S}_{\mathrm{theor}} = \Delta\tilde{S}_{\mathrm{theor}} - R[n(T) + Tn'(T)].$$

The resulting $\Delta\bar{S}_{\mathrm{theor}}$ values for both benzene and CB are smaller in magnitude than the $\Delta\bar{S}^{\mathrm{s}}$ values determined experimentally (see Tables 1 and 2). Thus it follows that the mobility of particles in the real adsorption layer is restricted with respect to that predicted by the ideal two-dimensional gas model.

The loss of mobility with increase in the Γ value can be characterized by the function $D = |\Delta\bar{S}^{\mathrm{s}}| - |\Delta\bar{S}_{\mathrm{theor}}|$. Strictly speaking, the function *D* also reflects the change in the adsorbent structure upon adsorption. However, the coverages studied were low (~0.001). If there exists bond rigidity in the crystal lattice, it becomes obvious that the change in the surface structure induced by adsorption would involve no more than 10^{-5}—10^{-4}% of the total adsorbent surface. Hence, it can be considered that the contribution of the change in the adsorbent entropy to the $\Delta\bar{S}^{\mathrm{s}}$ value would be negligibly small and interpretation of the function *D* in terms of the mobility of the adsorption layer is justified.

As the coverage of the surface increases, the *D* value decreases (Fig. 3). This is due to the fact that the molecules adsorbed first on the most active sites of the

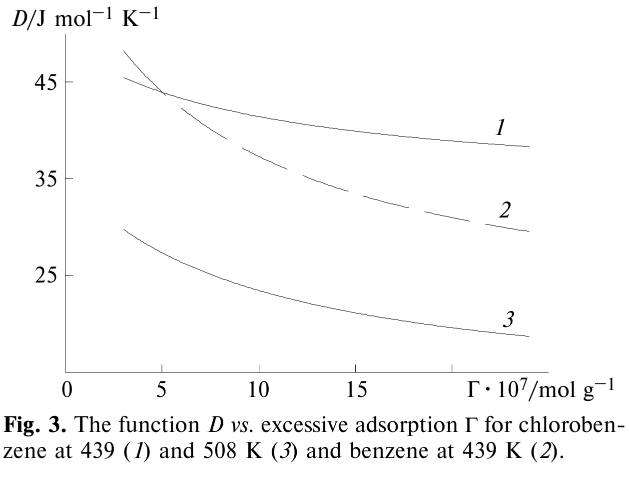

Fig. 3. The function *D vs.* excessive adsorption Γ for chlorobenzene at 439 (*1*) and 508 K (*3*) and benzene at 439 K (*2*).

surface are bound to the adsorbent more strongly than molecules adsorbed at greater coverages.

At T = 439 K, the decrease in the loss of molecular mobility of benzene with an increase in the surface coverage is more pronounced than that in the case of CB. This implies that various types of fixation on the surface are available for benzene. Conversely, in the case of CB, as the very active sites are occupied, the adsorbate molecules acquire approximately equal opportunities for fixing on the surface. Evidently, adsorbed benzene is more sensitive to the inhomogeneity of the alumina surface than chlorobenzene.

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