

9. V. F. Lysenkov, E. S. Platonov, and V. A. Rykov, "Singularities in the heat capacity at constant pressure in the critical region," in: Research and Design of Refrigeration Machines and Apparatus, Cryological Techniques, and Air Conditioning [in Russian], LTI (Lensoveta), Leningrad (1982).
10. I. M. Abdulagatov and B. G. Alibekov, "Equation of state of n-hexane, taking into account the scaling singularities near the critical point," Zh. Fiz. Khim., 56, No. 10, 2618-2619 (1982).
11. I. M. Abdulagatov and B. G. Alibekov, "Pseudospinodal curve method in the description of the scaling singularities near the critical point," Zh. Fiz. Khim., 57, No. 2, 468-470 (1983).
12. I. M. Abdulagatov and B. G. Alibekov, "Generalized equation of the $(C_p^* - \rho - \tau)$ surface of n-alkane in a wide region about the critical point," Zh. Fiz. Khim., 57, No. 2, 438-439 (1983).
13. O. B. Verbeke, "An equation for the vapor pressure curve," Cryogenics, 10, No. 6, 468-490 (1970).
14. C. M. Sorensen and M. D. Semon, "Scaling equation of state derived from the pseudospinodal," Phys. Rev. A, 21, No. 1, 340-346 (1980).
15. A. Michels, J. M. Levelt, and W. Graff, "Compressibility isotherms of argon at temperatures between -25°C and -155°C and at densities up to 640 Amaget (pressures of up to 1050 atm)," Physica, 24, No. 8, 659-671 (1958).
16. A. Michels, Hub. Wijker, and Hk. Wijker, "Isotherms of argon between 0°C and 150°C and pressures up to 2900 atm," Physica, 15, No. 7, 627-633 (1949).
17. M. A. Anisimov, B. A. Koval'chuk, V. A. Rabinovich, and V. A. Smirnov, "Experimental results on the heat capacity of argon in the single-phase and two-phase regions," in: Thermophysical Properties of Materials [in Russian], Standartov, No. 12 (1978), pp. 86-106.
18. V. A. Rabinovich and Yu. E. Sheludyak, "Method of constructing an equation of state in a wide region about the critical point," in: Physical Constants and Properties of Materials. Thermophysical Properties of Materials [in Russian], No. 16 (1982), pp. 108-124.

DENSITY OF ADSORBED WATER IN POWDER SYSTEMS. 3. $\gamma\text{-Al}_2\text{O}_3$

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The choice of dispersion medium is considered. Estimates are made of the density of water adsorbed on $\gamma\text{-Al}_2\text{O}_3$.

The measurement methods and techniques have been given in [1, 2]. The dispersion media were nitrobenzene and toluene. Figure 1 shows the results on the density of $\gamma\text{-Al}_2\text{O}_3$ as a function of water content.

There is a clear-cut effect on the density from the adsorbed water concentration in the dependence of the adsorbent mass or m/V relation (m is the mass of dehydrated adsorbent and V is the volume of the dispersed system).

The experiments showed that nitrobenzene is a liquid of zero effect in relation to $\gamma\text{-Al}_2\text{O}_3$, since the density of the dehydrated solid phase measured with this medium is independent of m/V . However, Fig. 1b shows that the density of the adsorbent in the same state as measured in toluene decreases as m/V increases, which indicates that the concentration of the liquid molecules in the surface layers of the dehydrated solid phase is less than in the bulk.

We now examine the changes in the relative densities of the dispersion media as affected by the water contents. The quantities are calculated from

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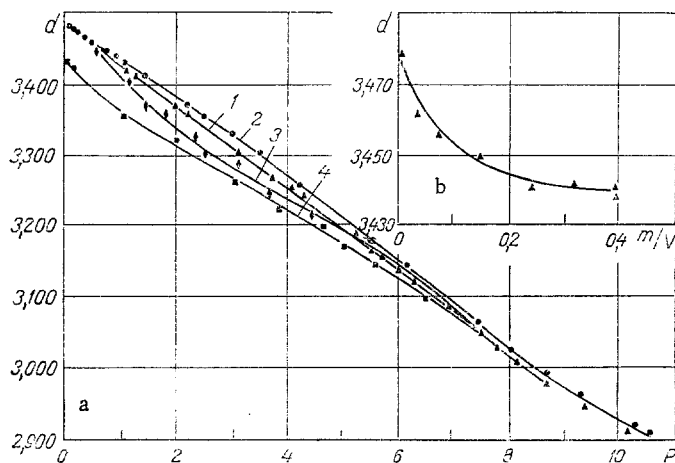


Fig. 1. Dependence of the density of $\gamma\text{-Al}_2\text{O}_3$ on the amount of adsorbed water for various values of m/V : a) measured in nitrobenzene: 1) $m/V = 0.195 \text{ g/cm}^3$, 0.029 ; 2) 0.0130 and in toluene; 3) 0.0130 ; 4) 0.195 ; b) measured in toluene for $P \rightarrow 0$; P at 1% was 0.56 mmole/g ; d in g/cm^3 and P in %.

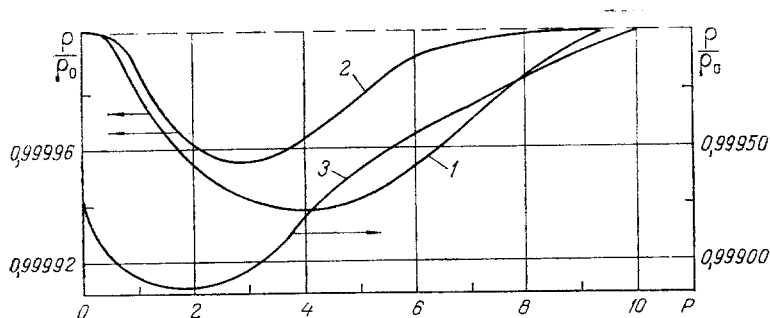


Fig. 2. Variation in the relative density of the dispersion medium as affected by the amount of water adsorbed on $\gamma\text{-Al}_2\text{O}_3$: 1) nitrobenzene for $m/V = 0.195 \text{ g/cm}^3$; 2) toluene for $m/V = 0.0130$; 3) toluene for $m/V = 0.195$.

$$\frac{\rho}{\rho_0} = \frac{\left(d - \frac{m}{V}\right) d'_0}{\left(d'_0 - \frac{m}{V}\right) d}, \quad (1)$$

where ρ/ρ_0 is the relative density change, d'_0 is the density of the hydrated specimen, ρ_0 is the density of the liquid corresponding to a critical mass of the solid phase, d is the density of the hydrated specimen, and ρ is the density of the liquid corresponding to a mass of solid greater than the critical value (d'_0 is measured with 1 g of powder, $m/V = 0.013 \text{ g/cm}^3$; curve 2 in Fig. 1).

Figure 2 shows that the density of the dispersion medium (nitrobenzene or toluene) is reduced in the water-content range corresponding to the formation of a double molecular adsorbed layer. We have considered in detail [1-8] the mechanism of this density change, where we have shown that the effects are determined by donor and acceptor groups on the adsorbent or in the dispersion medium.

The adsorption of nitrobenzene on $\gamma\text{-Al}_2\text{O}_3$ is due not only to charge transfer to the lattice (in that case, the electron donors in the molecule may be the oxygen atoms or the carbon atom next to the NO_2 group, while the lattice acceptor may be OH groups), but also to electrons being drawn off from the solid phase (in that case, the electron acceptors in the molecule are the nitrogen atom and the other carbon atoms, while the lattice donors are the oxygen atoms).

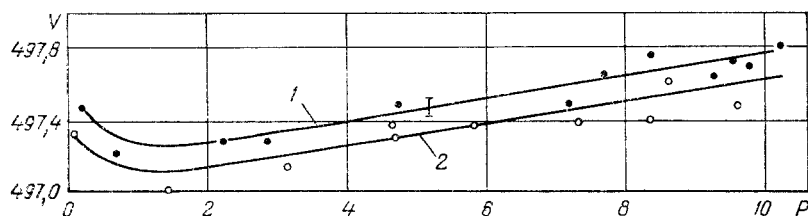


Fig. 3. Changes in unit-cell volume in $\gamma\text{-Al}_2\text{O}_3$ on adsorption: 1) of water; 2) of water and nitrobenzene; V in \AA^3 .

TABLE 1. Coordinates of Atoms in Active Centers in the Lattice of $\gamma\text{-Al}_2\text{O}_3$

Active center	Atoms in active center	Coordinates (\AA)		
		x	y	z
O_1H_1	O	0,9869	6,9081	0,0
	H	0,9869	6,9081	0,96
O_2H_2	O	0,9869	4,9344	1,9738
	H	0,9869	4,9344	2,9338
O_3H_3	O	0,9869	2,9606	0,0
	H	0,9869	2,9606	0,96
O_4H_4	O	2,9606	6,9081	1,9738
	H	2,9606	6,9081	2,9338
O_5H_5	O	2,9606	0,9869	0,0
	H	2,9606	0,9869	0,96
O_6H_6	O	4,9344	0,9869	1,9738
	H	4,9344	0,9869	2,9338
O_7H_7	O	6,9081	4,9344	0,0
	H	6,9081	4,9344	0,96
O_8H_8	O	6,9081	2,9606	1,9738
	H	6,9081	2,9606	2,9338
O_9H_9	O	6,9081	0,9869	0,0
	H	6,9081	0,9869	0,96
O_{10}	O	4,9344	6,9081	0,0
O_{11}	O	4,9344	2,9606	0,0
O_{12}	O	2,9606	4,9344	0,0

A single plane in the unit cell (Fig. 2 in [9]) in $\gamma\text{-Al}_2\text{O}_3$ can accommodate three molecules of nitrobenzene in the dehydrated state, which are oriented with their benzene rings perpendicular to the lattice surface and are attached as follows: the first to oxygen atom O_{12} , the second to the hydroxyl groups O_3H_3 and O_5H_5 , and the third to the hydroxyl groups O_6H_6 and O_8H_8 . Table 1 gives the coordinates of the lattice centers.

In the adsorption of the first water molecule at O_{10} and O_{11} , the nitrobenzene molecules occupy their former positions.

This very important feature explains why there is a horizontal part on curve 1 (Fig. 2), and determination of the boundaries to this part enables one to estimate the amount of bound water in group α (see [9]) and also in essence the density of the adsorbed water. There is also evidence for adsorption of the first groups of water molecules at the oxygen atoms from IR and NMR data [9, 10], and Fig. 3 indicates the deformation of the $\gamma\text{-Al}_2\text{O}_3$ lattice.

There is also an initial part due to lattice compression on the adsorption of water alone or with nitrobenzene, which indicates that the first groups of water molecules are attached to the oxygen atoms (charge transfer to the adsorbed molecules).

It has been shown [9, 10] that a second adsorbed water molecule (scheme 2 in the table of [10]) is attached to O_{12} and O_3H_3 , O_5H_5 in the $\gamma\text{-Al}_2\text{O}_3$ unit cell. As a result, two nitrobenzene molecules are displaced from the adsorption centers (the space is taken up by a double layer of adsorbed water molecules): the first being O_{12} and the second O_3H_3 , O_5H_5 , but the uncompensated hydrogen atom in a water molecule is an attachment center for a new nitrobenzene molecule within the double layer.

Consequently, the reduction in the number of molecules of dispersion medium in the full volume of this layer is responsible for reducing the relative density, as is observed.

The third and fourth adsorbed water molecules (during sorption) are attached, respectively, at the following centers: the third to O_2H_2 , O_4H_4 , and the fourth to O_6H_6 , O_8H_8 in the unit cell of scheme 3 (table of [10]), and they completely displace the nitrobenzene molecules

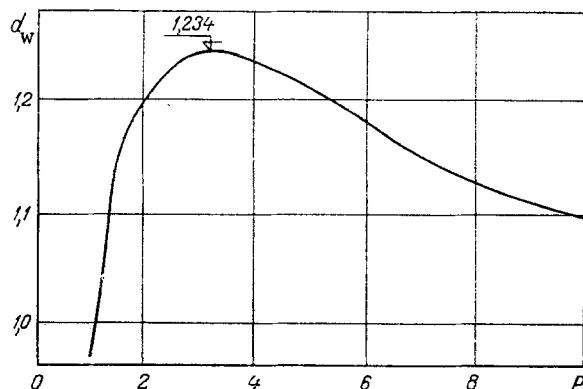


Fig. 4. Dependence of the density of water adsorbed on $\gamma\text{-Al}_2\text{O}_3$ on the amount as deduced with allowance for lattice deformation.

from the surfaces, but their uncompensated hydrogen atoms (in the water molecules) are new adsorption centers for two molecules of nitrobenzene, which occupy only part of the volume in the double molecular layer and project outward from the surface into the dispersion medium. Therefore, when four water molecules are adsorbed (4% water content), less than two nitrobenzenemolecules remain within the double molecular layer, which is responsible for the further reduction in the density of the dispersion medium.

The next stage involves the formation of water-molecule dimers, which greatly reduces the free space in the double molecular layer and therefore the measured mean density of the dispersion medium gradually approaches that of the normal liquid.

Toluene molecules are adsorbed also by charge transfer at the lattice (in that case, the electron donor in the molecule is the carbon atom in the ring joined to the CH_3 group, while the lattice acceptors are OH groups), and there is also electron extraction from the solid phase (here the electron acceptors are the other carbon atoms, while the lattice donors are oxygen atoms).

One plane in the unit cell of $\gamma\text{-Al}_2\text{O}_3$ in the dehydrated state can accommodate not three molecules (as in the case of nitrobenzene) but only two molecules of toluene. One of them has the plane of the benzene ring perpendicular to the lattice surface and is attached at the O_{12} center, while the other has it parallel to the surface and is attached to O_6H_6 . The parallel orientation is responsible for a C-OH bond, and here lies the difference in adsorption mechanism between toluene and nitrobenzene. However, there is still a reduced concentration of dispersion-medium molecules (toluene) in the surface layer even in the dehydrated state.

It is readily shown that water sorption increases the density reduction in the dispersion medium within the double-layer limits, and consequently a liquid with a nonzero effect in relation to the dehydrated phase cannot be used to estimate the density of the adsorbed water, as is evident from Figs. 1 and 2.

We can calculate the density of the adsorbed water with allowance for the lattice deformation as follows from the density distribution for hydrated $\gamma\text{-Al}_2\text{O}_3$ found for the critical mass of adsorbent (here 1 g):

$$d_w = \frac{0.01(P - P_0) d d_0 \frac{V_0}{V_i}}{0.01 P d_0 \frac{V_0}{V_i} + d_0 \frac{V_0}{V_i} - d}, \quad (2)$$

where d_w is the density of the adsorbed water, P is the adsorbed water content in %, P_0 is the amount of water corresponding to the first adsorbed molecules, where there is as yet no density change in the dispersion, so in our case $P_0 = 0.5\%$; d_0 is the density of the adsorbent measured at P_0 ; d is the density of the adsorbent measured at P ; and V_i and V_0 are the unit-cell volumes of $\gamma\text{-Al}_2\text{O}_3$ recorded respectively with P and P_0 during the adsorption of water and nitrobenzene.

We have shown [10] that P_0 corresponds to rigid attachment of molecules adsorbed in scheme 1 (see table in [10]) and that these molecules relate to group a , which is not linked to the rest of the ensemble.

Figure 4 shows the density of water adsorbed on $\gamma\text{-Al}_2\text{O}_3$ as a function of the amount, where there is a maximum of 1.236 g/cm^3 at 3-4% water content.

In essence, this density distribution is similar to that found for kaolinite [5], but in that case the maximum density virtually corresponds to the completion of the double molecular layer P_m , while with $\gamma\text{-Al}_2\text{O}_3$ the density at the time of double-layer formation is 1.1 g/cm^3 .

These differences are due to the following factors. In kaolinite, a dimer (a structure element in the double molecular layer) is mainly adsorbed simultaneously at an OH group and an oxygen atom.

The adsorption energy at these centers is considerable [5, 11], and the centers initiate electron-density redistribution in the $(\text{H}_2\text{O})_2$ system such that the hydrogen bond in it is strengthened by comparison with the isolated dimer.

The strengthened hydrogen bond reduces the distance between the oxygen atoms and consequently increases the density of the adsorbed water.

When the double molecular layer is completed on $\gamma\text{-Al}_2\text{O}_3$, only one fifth of the dimers are similar in structure to the dimers formed on kaolinite, while 80% are adsorbed at two OH groups each (scheme 3 in the table of [10]).

The energies of such bonds are half those of bonds formed under scheme 2, and so the energies of the hydrogen bonds between the water molecules in the adsorbed dimers approximate to the value for normal liquid water, and the same applies to the distances between the atoms and the density of the material distributed in the dimers, as is found by experiment.

LITERATURE CITED

1. P. P. Olodovskii, M. G. Murashko, and V. A. Zazulov, "The structure of water adsorbed in dispersed systems of complicated mineral composition," *Inzh.-Fiz. Zh.*, 35, No. 6, 1107-1116 (1978).
2. P. P. Olodovskii and L. A. Malkova, "Deformation of the solid phase in a dispersed system produced by adsorbed water and organic compounds," *Inzh.-Fiz. Zh.*, 40, No. 2, 304-312 (1981).
3. P. P. Olodovskii and M. G. Murashko, "Density change in the dispersion medium in relation to solid-phase concentration in a solid-liquid system," *Inzh.-Fiz. Zh.*, 21, No. 5, 868-875 (1971).
4. P. P. Olodovskii, "The dispersion-medium density-change effect in a solid-adsorbed water-liquid system: calculation of adsorption characteristics for dispersed systems," *Inzh.-Fiz. Zh.*, 26, No. 4, 604-612 (1974).
5. P. P. Olodovskii, "The density of adsorbed water in dispersed systems," *Inzh.-Fiz. Zh.*, 40, No. 4, 711-716 (1981).
6. P. P. Olodovskii, "Effects of surface properties in a hydrated solid phase on the dispersion-medium density-change effect," *Inzh.-Fiz. Zh.*, 26, No. 3, 701-713 (1977).
7. P. P. Olodovskii and L. A. Malkova, "A study of the structural parameters of surface layers in dispersed systems by estimating the dispersion-medium density and the solid-phase lattice deformations," *Inzh.-Fiz. Zh.*, 46, No. 5, 746-654 (1984).
8. P. P. Olodovskii, "The density of adsorbed water in dispersed systems. Part 2. Montmorillonite," *Inzh.-Fiz. Zh.*, 46, No. 6, 938-942 (1984).
9. P. P. Olodovskii and S. A. Kumashov, "Evaluating the structure of adsorbed water in dispersed systems by NMR spectroscopy. Part 1. $\gamma\text{-Al}_2\text{O}_3$," *Inzh.-Fiz. Zh.*, 48, No. 3, 467-472 (1985).
10. P. P. Olodovskii and G. A. Ivkovskaya, "Estimating the binding energies of adsorbed water molecules on the surfaces of solids in dispersed systems by IR spectroscopy. Part 3. $\gamma\text{-Al}_2\text{O}_3$," *Inzh.-Fiz. Zh.*, 47, No. 1, 111-116 (1984).
11. P. P. Olodovskii, "Evaluating the structure changes in adsorbed water in dispersed systems during hydration by IR spectroscopy," *Inzh.-Fiz. Zh.*, 40, No. 3, 447-454 (1981).