

Study of the effect of surface chemistry and adsorbent texture on adsorption isotherms by comparative method

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Abstract - The development of A.V. Kiselev's method of absolute adsorption values into modern comparative methods has been shown. These latter differ in only the choice of coordinates of comparative plots, the analysis results being identical. Based on a comparison of the known standard nitrogen adsorption isotherms and adsorption measurements for high P/P_0 , a generalized standard isotherm for $P/P_0 = 0.1-0.99$ has been proposed. The comparative method has been applied for the determination of texture parameters of a series of adsorbents and catalysts and for the study of the dependence of their adsorption properties on chemical nature of the surface.

1. A. V. KISELEV'S METHOD OF ABSOLUTE ADSORPTION VALUES

A.V. Kiselev was one of the first scientists who almost 40 years ago clearly distinguished between the effects of geometric (adsorbent texture) and chemical (surface nature) factors on adsorption properties. For this purpose Kiselev and co-workers proposed the method of absolute adsorption values [1] in which adsorption was calculated per unit surface of the adsorbent rather than per unit mass, as had been commonly adopted.

The surface area was demonstrated to be the determining factor for physical adsorption. Changes of the surface area in real systems by 3-4 orders of magnitude lead to the same changes of the adsorption value. The influence of the surface chemical nature on physical adsorption is much less because of its low specificity. The absolute value of adsorption for a certain adsorptive and certain conditions changes 1.5-2 times at most and several times in some exceptional cases upon varying the surface nature. One of Kiselev's co-workers - K.D. Shcherbakova has especially studied these cases by chemically modifying the surface of silica gel by the various methods. Together with R.S. Petrova, she has found a 1.5 times decrease in the absolute adsorption value for crypton on silica gel modified with trimethylchlorosilane. The change in surface nature of adsorbents due to the change in the degree of hydroxylation is more usual. E.V. Khrapova has found that nitrogen adsorption on a dehydroxylated silica gel is 20-25% less than on a hydroxylated one. The chemical nature of the surface has larger effect on adsorption of organic substances and water. Kiselev's colleague N.N. Avgul has shown that destruction of surface complexes upon calcination of carbon blacks results in a several times change of water and methanol adsorption.

Regarding the effect of texture, the method of absolute adsorption values (Fig. 1) has made it possible to show, e.g., the identity of adsorption properties of non-porous quartz (middle curve), large- and fine-pore aluminosilica gels in the initial region of the isotherm and their difference in the following region due either to pure geometric restrictions in fine pores or to the process of capillary condensation in large pores. Now let us consider until what pore sizes diminution this identity is observed for fine pores, i.e. when the increase in adsorption potential in them starts to reveal. The method of absolute adsorption values has yielded unambiguous results for adsorption of large molecules. An increase in absolute values of their adsorption has been observed even at a pore diameter of 2-3 nm. For example, for heptane adsorption on silica gel (Fig. 2) these data are considered to be quite reliable, since its surface area, necessary for the calculation of absolute values of adsorption, could be assessed using much smaller molecules of nitrogen or methanol. The situation was worse when the effect of pore narrowing on adsorption of small molecules was examined. In this instance, the surface area of micropores could not be determined for the known reasons, and Kiselev suggested that, instead of absolute values,

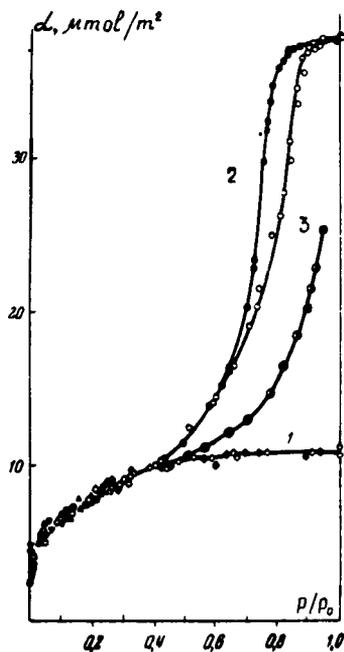


Fig. 1. Isotherms of absolute adsorption values for methanol on fine-porous (1) and large-porous (2) aluminosilica gel and on non-porous quartz (3) [1].

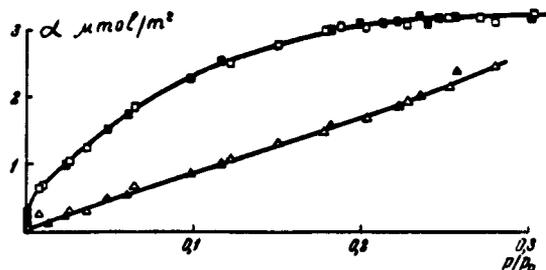


Fig. 2. Isotherms of absolute adsorption values for heptane on large-porous (triangles) and fine-porous (squares) silica gels [1].

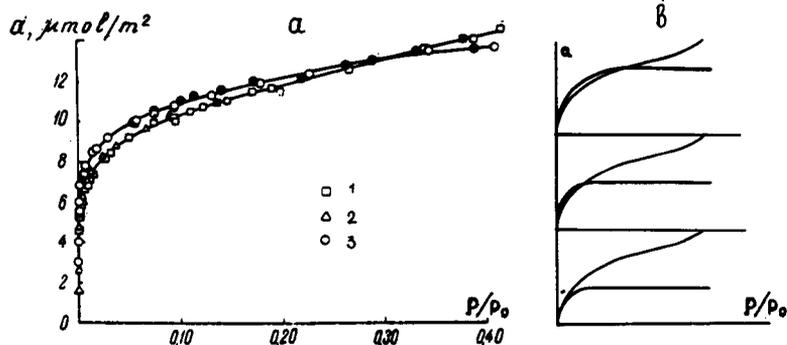


Fig. 3. a) Isotherms of absolute adsorption values on quartz (1), large-porous silica gel (2), and microporous silica gel (3); b) scheme of arbitrary matching of isotherms at different P/P_0 . The contact points of particles in a large-porous SiO_2 have been grown over upon ageing.

adsorption isotherms be compared by their matching in any arbitrary point. E.g., in [2] nitrogen adsorption isotherms for ultramicroporous silica gel No 8 and for quartz were matched at $P/P_0 = 0.3$ (Fig. 3). Thus, a conclusion was made that the adsorption potential with respect to nitrogen increases even for the pores of 2.4nm in size and, for this reason, the isotherm for silica gel was steeper than that for quartz up to the pressure indicated. It is clear now (right-hand side of the fig.3) that by choosing different arbitrary matching points one obtains an arbitrary difference in the form of isotherms and, consequently, an arbitrary interpretation of the role of increasing of adsorption potential. This contradicts modern theoretical calculations and experimental estimates of the heats of adsorption. A more correct interpretation can be given on the basis of modern comparative methods according to which isotherms are matched in some interval of adsorption values rather than in one point. Besides, in this case assessment of surface areas of samples under study is not necessary.

2. MODERN COMPARATIVE METHODS

These methods are based on comparative plots with one axis corresponding to adsorption values for the reference sample and the other to those of the sample under study. It should be noted that such a unique approach was first proposed by Dubinin and Zaverina in 1954 [3], however, that work remained unnoticed and the later work by de Boer and Lippens [4], who developed the so-called t -method in 1965, is considered to be pioneering in the literature. Later on Pierce [5] and Sing [6] proposed their own versions. Sing's version called α -method, is widely used in investigations. In our laboratory [7], an alternative comparative method has been proposed. According to this absolute adsorption values in moles per square meter for the reference are plotted as abscissa against adsorption in moles per gram for the sample under study as ordinate. A mathematical analysis of all the versions of the comparative method [8] indicates that they differ in only the choice of values plotted as coordinates of comparative plots; results of a comparative analysis being almost the same for these versions. Our method seems to be closer to Kiselev's method than the others because we plot absolute adsorption values as abscissa.

3. GENERALIZED STANDARD NITROGEN ADSORPTION ISOTHERM

For any comparative method the choice of a reference is very important. Of course, the choice depends upon the aim of the study. For texture studies a reference and a tested sample must have the same chemical nature and, in a more general case, the same absolute adsorption properties over a certain interval. For the investigation of the effect of chemical nature the sample must have the same texture as the reference or, at least, should have no micropores that distort the shape of isotherms in the monomolecular region.

We have compared isotherms of absolute adsorption values of nitrogen for almost all available standard samples. It is seen in Fig. 4 that all isotherms, except for de Boer's one, lie within a narrow band. Neglecting de Boer's isotherm in our consideration, we have obtained an averaged isotherm for P/P_0 0.1-0.75 which is close to the known Sing's isotherm for oxides [9]. In addition, having examined nitrogen adsorption over 15 coarsely dispersed systems with a surface area of 0.3-1.5 m^2/g [10], we have superstructured this isotherm for the region of high P/P_0 up to 0.99 and obtained eventually a generalized standard isotherm for P/P_0 0.1-0.99 suitable for solution of many texture problems. Such an isotherm is described by the following equation:

$$\alpha = A_0 + A_1 b + A_2 b^2 + A_3 b^3 + A_4 b^4 + A_5 b^5 \mu \text{mole}/m^2,$$

where $b = \ln(P/P_0)$. Coefficients for this equation are listed in Table 1.

TABLE 1.

| P/P_0 interval | A_0 | A_1 | A_2 | A_3 | A_4 | A_5 |
|------------------|---------|---------|---------|----------------------|-----------------------|-----------------------|
| 0.10-0.60 | 26.8546 | 22.0027 | 14.2650 | 4.2531 | 0.24743 | -0.10715 |
| 0.10-0.60 | 27.1667 | 23.4490 | 16.7500 | 6.5135 | 0.9971 | 0 |
| 0.55-0.92 | 46.5644 | 242.443 | 1120.65 | 2884.45 | 3729.22 | 1890.90 |
| 0.90-0.99 | 119.463 | 4983.14 | 130098 | 1792·10 ³ | 12438·10 ³ | 34279·10 ³ |

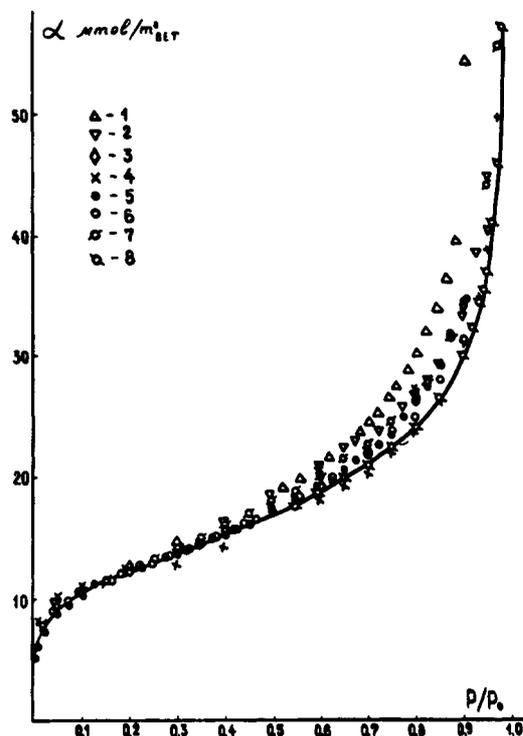


Fig. 4. Isotherms of absolute adsorption values for nitrogen on various standard samples: 1 - abstracted from [15]; 2 - from [16], 4 - from [5]; 5 - from [17], 6 - from [9]; 7 - from [2]; 8 - from [10]; dotted line indicates a generalized standard isotherm.

In the comparative plot (Fig. 5), a generalized standard isotherms (abscissa) is compared to some other standard isotherms (ordinate). In the region of high P/P₀ they go upwards apparently due to a small contribution of capillary condensation.

To study micropores whose filling in the case of nitrogen is completed at P/P₀ = 0.01 or less, when the effect of the chemical surface nature may occur it is necessary to use the reference sample with adsorption properties close to those characteristic of this region. The choice of this reference sample is rather complicated and, criterion commonly used by Sing and by us is identity of the chemical nature, though some difficulties may arise due to the presence of contaminants or modifying additives on the surface.

In our works the comparative method finds wide application for solving texture problems (geometric aspect) and studying the effect of the surface nature on adsorption (chemical aspects).

4. GEOMETRIC ASPECT

In [7] we have advanced an approach to the estimation of the role of the increase in adsorption potential in ultramicropores with application of the comparative method. Figure 6 presents a comparative plot of silica gel No 8 (upper curve). The plot was found to consist of two linear parts. The upper line corresponds to affinity of isotherm of nitrogen adsorption over this silica gel and quartz beginning from P/P₀ = 0.001. The lower steeper part is related to a steeper isotherm of adsorption in ultramicropores. The calculations indicate that, firstly, ultramicropores are the regions around points of contact of silica gel globules; adsorption capacity of these micropores determined from intercept

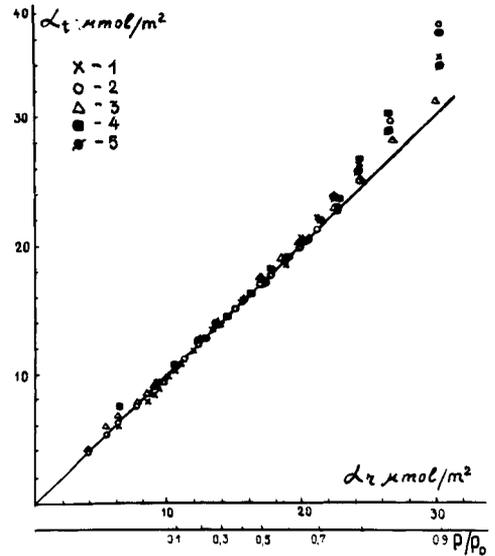


Fig. 5. Comparison of the generalized standard isotherm (abscissa) with isotherms 1 from ref. [9], 2 from ref. [17], 3 from ref. [18], 4 from ref. [19], and 5 from ref. [5] (ordinate).

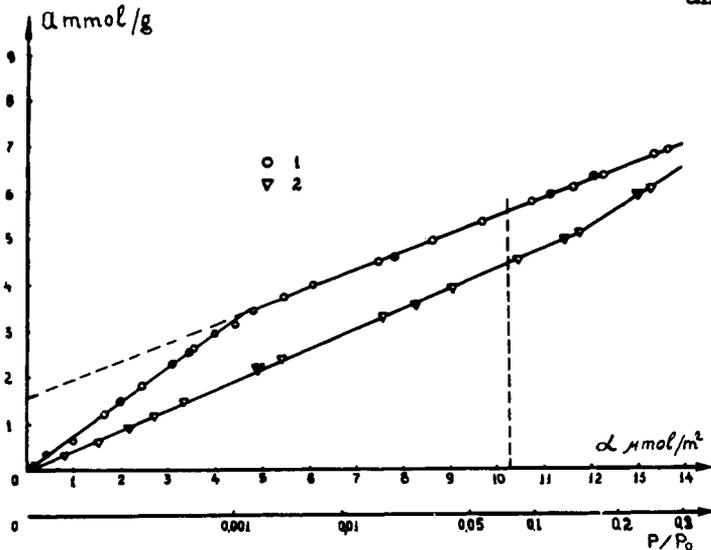


Fig. 6

Fig. 6. Comparative plot for nitrogen adsorption on microporous (1) and large-porous (2) silica gels. In (2) the contact points of particles have been grown over upon ageing [7]. A vertical dotted line corresponds to a monolayer.

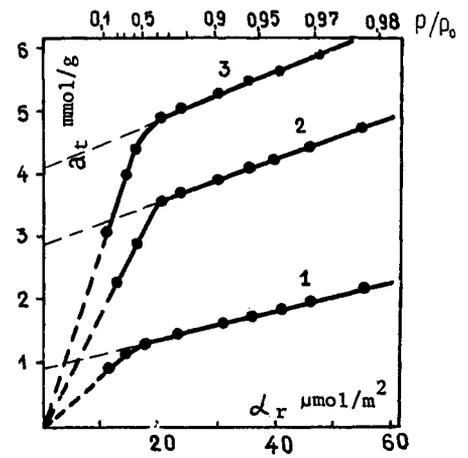


Fig. 7

Fig. 7. Comparative plot for nitrogen adsorption on carbons with increasing (1-3) activation degree

corresponds to the number of molecules in a monomolecular chain around this region. Secondly, density of molecules package in this chain at the given P/P_0 is twofold higher than over the rest surface of globules (where absolute adsorption is nearly the same as over the quartz surface). Thirdly, both the surface area of microporous ($350 \text{ m}^2/\text{g}$) and the surface area beyond them ($380 \text{ m}^2/\text{g}$) are estimated from inclination of the first and second linear parts and calculations according to the globular model.

The comparative method has also been used to study changes in the texture of carbon materials occurring during their activation (Fig. 7). Since the comparative plots break at $P/P_0 = 0.5$ and extrapolation lines of their left parts pass practically through the origin, an assumption has been made that such type of carbons has insignificant volume of ultramicropores. This part of plots is attributed to a total nitrogen adsorption in supermicropores and mesopores, and the right linear part to adsorption in mesopores only. Although mechanisms of cooperative adsorption in supermicropores and adsorption over the reference sample are different (as shown by Sing [11]), nevertheless, at the first step adsorption in supermicropores takes place on their walls likewise adsorption over the reference sample. This allows one to determine the total surface area and the surface of mesopores from

TABLE 2.

| Nos | % burn off | A m^2/g | A_{me} m^2/g | A_{smi} m^2/g | V_{smi} cm^3/g |
|-----|------------|-------------------------|--------------------------------|---------------------------------|----------------------------------|
| 1 | 3.1 | 21.1 \pm 0.9 | 23.2 \pm 0.9 | 0 | 0.007 |
| 2 | 5.6 | 38.8 \pm 0.03 | 26.4 \pm 1.5 | 12.4 | 0.026 |
| 3 | 9.3 | 91.8 \pm 8.4 | 24.9 \pm 1.5 | 66.9 | 0.075 |
| 4 | 13.1 | 117.4 \pm 9.1 | 28.0 \pm 1.8 | 89.4 | 0.082 |
| 5 | 16.5 | 172.5 \pm 9.5 | 30.1 \pm 1.4 | 142.4 | 0.111 |
| 6 | 18.5 | 211.9 \pm 7.5 | 29.0 \pm 2.6 | 182.9 | 0.131 |
| 7 | 20.8 | 259.8 \pm 3.6 | 29.4 \pm 1.9 | 230.4 | 0.159 |

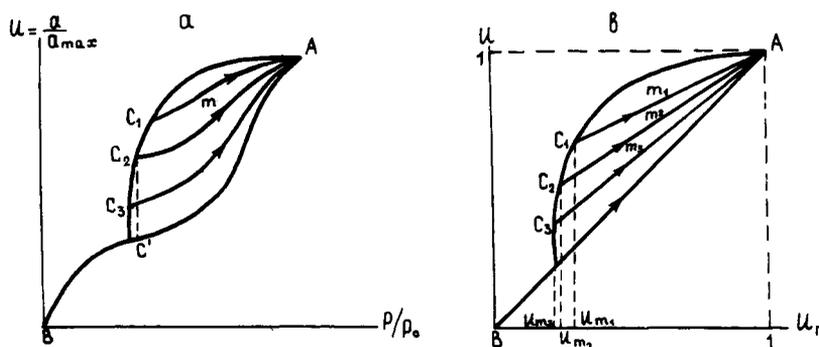


Fig. 8. a) Capillary-condensation hysteresis loop with scanning curves, b) comparative plot for this loop (scheme).

the slope of the left- and right parts of the plots, respectively, and the surface of supermicropores from their difference. As seen in Table 2, during activation the surface of supermicropores and their volume increase drastically unlike the surface of mesopores.

The scanning of the region of capillary condensation hysteresis has been studied by the comparative method [12]. Adsorption in the boundary adsorption branch is plotted as abscissa and adsorption scanning curves as ordinate. The shape of comparative plots is presented in Fig. 8. Adsorption isotherms of scanning branches and the boundary branch were found to be affine, which means that adsorption in a partially filled porous system occurs similarly to adsorption in an unfilled system within the same pressure interval. This permits one to calculate in more detail the distribution of cavities and throats in porous solids [12].

One more field of application of the comparative method appears to be studying of supported metal catalysts. Metal dispersity in them is determined by chemisorption which is significant over metal and negligible (or might be taken into account) over support. An example of such a determination of

dispersity of Ir over alumina by the comparative method is shown in Fig. 9 [13]. Hydrogen chemisorption over Ir black with the known surface area is plotted as abscissa, hydrogen chemisorption over three samples with supported Ir is given as ordinate. The inclination of lines provides average metal dispersity as a ratio of the amount of surface metal atoms to the total amount of atoms in the particle.

5. CHEMICAL ASPECT

The works devoted to the study of the effect of surface chemical nature on physical adsorption by the comparative method appear rather rarely in the literature. The simplest method to change this nature is its physical or chemical modification by means of adsorption of different substances whereas texture parameters remain practically the same.

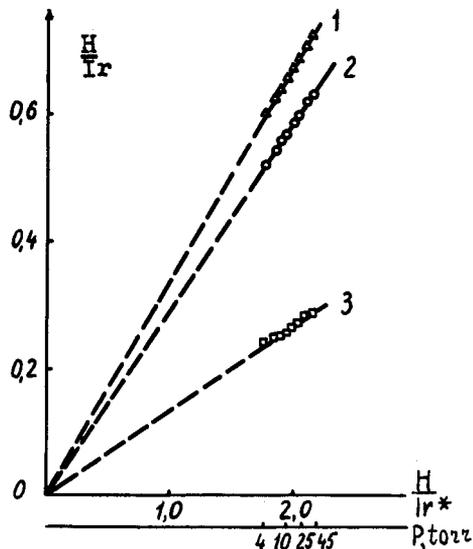


Fig. 9. Comparative plot for hydrogen chemisorption on three samples of supported Ir. Abscissa - hydrogen chemisorption on Ir black. Ir dispersity in samples: 1 - 0.35, 2 - 0.30, and 3 - 0.14

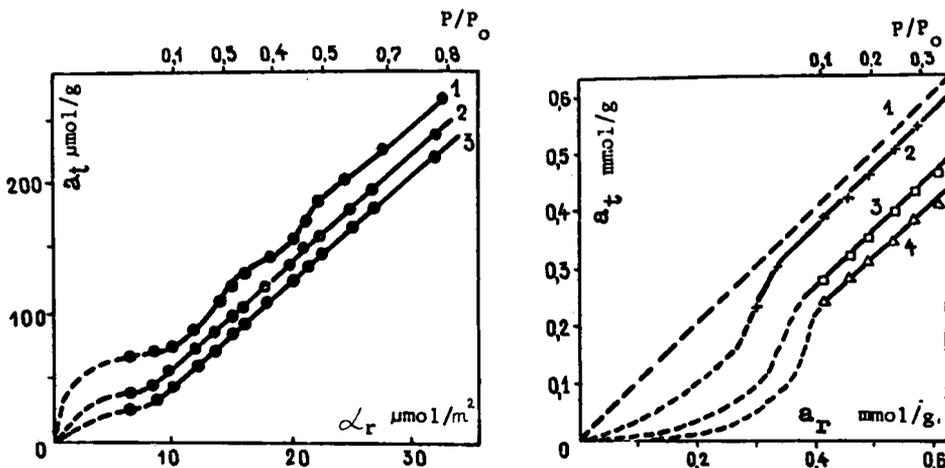


Fig. 10. Comparative plot for nitrogen adsorption on graphitized black modified with polysiloxane. 1 - initial sample, 2,3 - samples with coverages 0.5 and 1.0 monolayer (based on data from ref. [10]). Fig. 11. Comparative plot for nitrogen adsorption on carbon black modified with methanol. Abscissa - initial sample, 2,3,4 - samples with coverages 0.15, 0.8 and 1.3 monolayer (based on data from ref. [13]).

Fig. 10 shows a change in the shape of comparative plots of nitrogen adsorption over graphitized carbon black as a result of sequential modification of its surface with polysiloxane [10]. A wave-like plot for the initial sample is smoothing as the surface is covered with the modifying agent; nitrogen adsorption herein decreases while the plots in a farther region remain parallel, which confirms stability of the surface area.

A similar plot (Fig. 11) has been obtained by application of comparative method to experimental results of Dubinin et al. [14] of physical modification of graphitized carbon black with methanol. Here as well the increasing amount of modifying agent decreases nitrogen adsorption but inclination of the comparative plots in the polymolecular region remains constant, which also confirms constancy of the surface area at modification. Note that the surface determined by the BET method decreases monotonously at modification due to erroneous application of a constant standard molecular surface area of 0.162 nm^2 in the cases where it actually increases at modification.

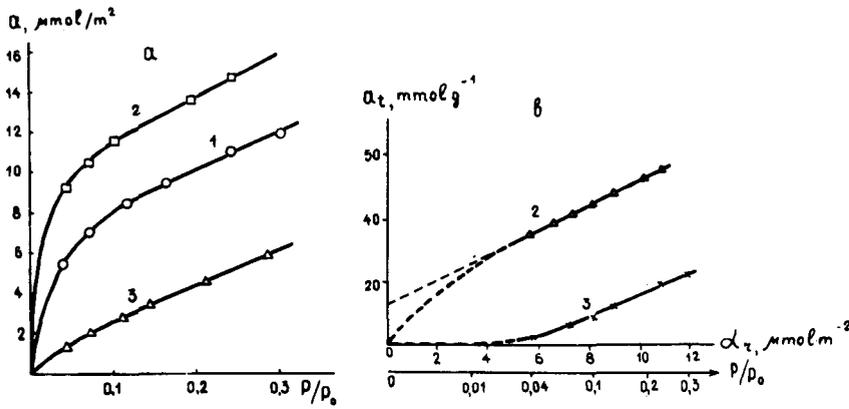


Fig. 12. a) Isotherms of absolute adsorption values for argon on silica gel (1), corundum (2) and polypropylene (3) (based on data from ref. [14]) b) comparative plot for (2) and (3) if adsorption on (1) is plotted as abscissa.

In the left of Fig. 12 isotherms of absolute values of Ar adsorption on corundum, silica gel and polypropylene are shown. Isotherms of adsorption over corundum are steeper and on polypropylene smoother than on silica gel. If we plot the isotherm on silica gel as abscissa (Fig. 12, right part), then the curves for the corundum and polypropylene are convex and concave, respectively; in the polymolecular region however, these curves became straight which indicates affinity of isotherms. From the slope of these linear parts surface areas of the samples have been determined, which for corundum appeared to be by 17% lower than those calculated by the BET method, and for polypropylene by 28% higher. This means that the standard molecular surface area $a_m = 0.18 \text{ nm}^2$ should be corrected for all above cases. Actual values of a_m for a denser packing of Ar molecules over corundum are 0.15 nm^2 and for a looser one over polypropylene 0.23 nm^2 [15].

A comparison of nitrogen adsorption over BaSO_4 and aluminosilica gel with adsorption over silica gel (abscissa) is shown in Fig. 13. For aluminosilica gel the comparative plot is linear over the whole pressure region and passes through

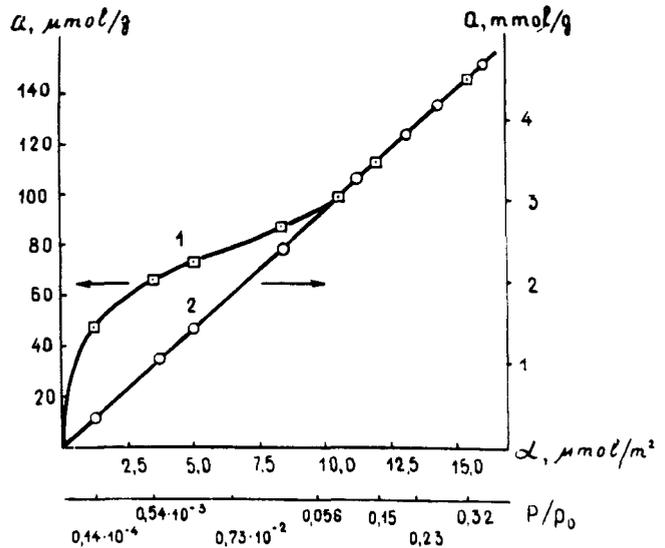


Fig. 13. Comparative plot for nitrogen adsorption on BaSO_4 (1) and aluminosilica gel (2): Adsorption on silica gel is plotted as abscissa (based on data from ref. [1]).

the origin which indicates complete affinity of their isotherms; for BaSO_4 the plot is first convex (denser molecules packing in the monomolecular region) and then transforms into a straight line in the polymolecular region, i.e. shielding of a force field of this ionic adsorbent results in adsorption similar to that for silica gel.

6. CONCLUSIONS

Most of adsorption studies and texture investigations of adsorbents and catalysts are aimed at a comparison of adsorption properties of different adsorbents over various solids as well as of changes of their texture under the action of chemical, thermal or mechanical effects. There is no exaggeration in saying that A.V. Kiselev was the first to pose this problem and to make successful attempts to solve it. The comparative methods that have been developed in the last decades provide unambiguous comparisons and allow detection of occurring changes. It is demonstrated in this work that, although all these methods differ in the values applied, they are fundamentally close.

When it is needed to obtain absolute texture parameters of porous and dispersed solids, a substantiated choice of the reference sample and its detailed study by a complex of different methods are important. After standard isotherms known from the literature have been compared and additional measurements over extremely coarsely dispersed non-porous systems have been made, a generalized standard isotherm for a broad interval of P/P₀ from 0.1 to 0.99 is proposed. Potentialities of the comparative methods are illustrated by studies of the texture of adsorbents and catalysts as well as by studies of the effect of their-chemical nature on adsorption properties.

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