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Adsorption of Aliphatic Alcohols, Alkanoic Acids and Acetone on the Silica Surface: Chemical and Steric Factors of Monolayer Formation; Apparent Fractal Dimension

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ADSORPTION OF ALIPHATIC ALCOHOLS, ALKANOIC ACIDS AND ACETONE ON THE SILICA SURFACE: CHEMICAL AND STERIC FACTORS OF MONOLAYER FORMATION; APPARENT FRACTAL DIMENSION.

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Abstract In this communication we made a detailed and critical analysis of the factors which may lead to mistakes in measuring the number of molecules in monolayer on the surface of different silica gels, when using aliphatic alcohols, alkanoic acids and acetone as adsorbates. The chemical factor is due to the complex interaction of alcohol (acid) molecules with the surface hydroxy groups of different reactivity. This results in a two-steped form of adsorption isotherms studied by IR technique. The steric factor is connected with the peculiarities of packing adsorbate molecules on the surface of micropores, if one takes into consideration the intrinsic volume of the molecules. As a result, the apparent fractal dimension ($D_a > 2$) of the surface can be introduced, even if the adsorbent surface has no irregularities of the atomic scale size. This effect was shown by simulation of adsorption on the surface of Menger sponge. Based on the analysis mentioned above, an accurate method for measuring monolayer adsorption and surface fractal dimension was suggested.

INTRODUCTION

Studying of forming monolayer on the surface of dispersed solids during adsorption gives information about their structure, mechanism of adsorption, interaction in the adsorbed monolayer, etc. A common method for measuring the specific surface area S_{sp} is based on measuring the monolayer adsorption.[1,2] The S_{sp} value can be calculated from the number N of molecules absorbed by 1 g of the adsorbent to form monolayer, and the cross-sectional area σ of adsorbed molecules: $S_{sp} = N * \sigma$. Generally, the function $N(\sigma)$

is dependent on the fractal surface dimension D:[3,4]

$$N \sim \sigma^{-D/2} \quad . \qquad (1)$$

Fractal dimension D of the surface characterizes its roughness and varies from 2 for smooth surface to 3 for completely rough and irregular surface. The value of D can be determined experimentally from Eq.(1). To do this, one measures the monolayer adsorption of different adsorbates, usually belonging to one class of compounds (for example, aliphatic alcohols or alkanoic acids), and calculates D from the slope of the straight line lnN ($ln\sigma$). In this paper we discuss several peculiarities of forming adsorbed monolayer by aliphatic alcohols, alkanoic acids, and acetone on the surface of different silica gels. Since for these systems, the cases of large $D > 3$ values (that has no physical meaning) were reported in the literature[5,6], a detailed analysis of adsorption was carried out. We define two factors - chemical factor and steric factor, which influence adsorption measurements, and, as a result, the value of D.

EXPERIMENTAL

Adsorption measurements were carried out on commercial silica gels of the KSM-6, KSS-3, KSS-4, and KSK-2 types (ex-USSR). The surface areas measured by the low temperature adsorption of argon (σ = 17.6 $Å^2$) were 550, 520, 680 and 375 m^2/g, correspondingly. Before the adsorption experiments samples were dried at 120°C or 700°C for 7-8 hours.

n-Aliphatic alcohols (CH_3OH, C_2H_5OH, C_3H_7OH, $C_7H_{15}OH$, $C_{10}H_{21}OH$) and n-alkanoic acids (acetic, pentanoic, and octanoic) were adsorbed from their solutions in CCl_4 and C_2Cl_4 (no effect of the solvent nature has been found). The amount of adsorbed compound was determined from the decrease of its concentration in solution by measuring the intensity of C-H vibration line in its IR absorption spectrum (ν

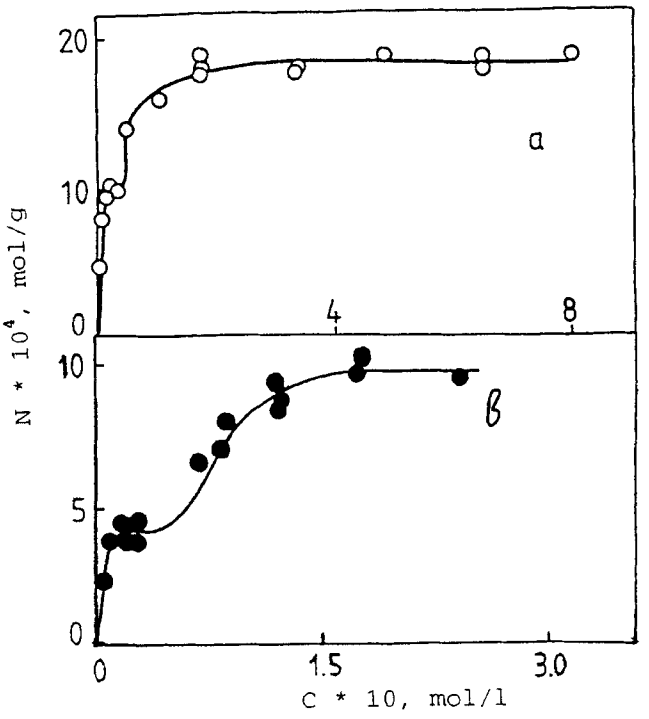

FIGURE 1 Adsorption isotherms for a) octanoic acid and b) gexanol-1 on silica gel KSK-2 from their solutions in CCl_4 (T = 18°C; C - equilibrium concentration of the adsorbate).

= 2975 cm^{-1}, 2920 cm^{-1}, 3005 cm^{-1} for alcohols, acids, and acetone respectively). Values of adsorption sites were taken from ref.[7,8]. Benzene (σ = 43.0 $Å^2$) was adsorbed from its solution in hexane. Adsorption isotherms of benzene were measured using refractometric method.[10]

RESULTS AND DISCUSSION

The isotherms of adsorption of aliphatic alcohols, alkanoic acids, and acetone at 18°C on the surface of silica gels of different pore structure are presented at Figures 1,2. All these isotherms, obtained at the range of concent-

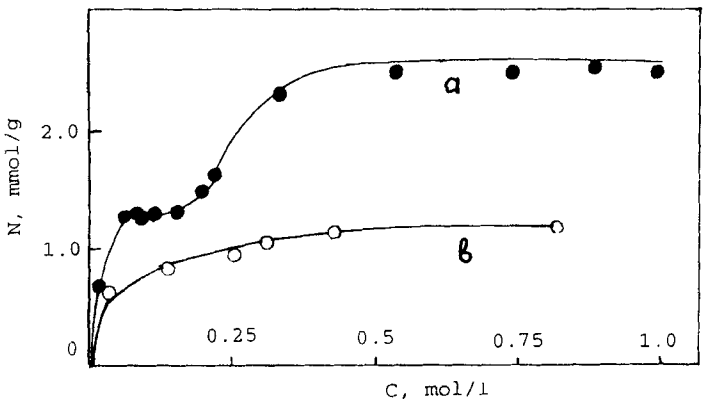

FIGURE 2 Adsorption isotherms for acetone on KSS-3 silica gel samples at 18°C: a) calcinated at 120°C; b) calcinated at 700°C (C - equilibrium concentration of acetone).

rations 0 - 1.5 mol/l, exhibit two distinct plateaus. The first plateau, seen at the range of concentrations 10^{-1} - 10^{-2} mol/l, corresponds to 40-50% filling of the surface measured by argon adsorption (BET method). If then one takes these values as corresponding to the monolayer ad-

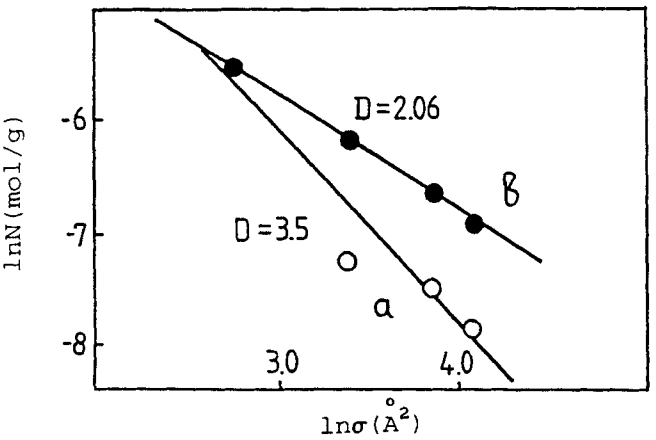

FIGURE 3 Determination of the fractal dimension of KSK-2 silica gel according to argon and acids adsorption: a) calculated from the first plateaus, b) calculated from the second plateaus of adsorption isotherms.

sorption of organic molecules and substitutes the obtained values of N in equation (1), the anomalous high fractal dimensions D = 3.5 - 4.5, contradictory to the fractal geometry, are obtained from the slope of lines lnN (lnν) (Figure 3,a). The same procedure, repeated for the second plateau, gives 70-95% filling of argon corresponding surface and fractal dimensions D = 2.05, 2.50, 2.35, 2.60 $\pm$ 0.1 for silica gels KSK-2, KSS-4, KSS-3, and KSM-6 respectively (see Figure 3,b for KSK-2). We note that adsorption isotherms of alcohols and acids on dispersed aluminum oxide (type IC-02, S_{Ar} = 195 m^2/g) exhibit one plateau, corresponding values of N giving D = 1.9 $\pm$ 0.1.

Chemical factor

It is reasonable to suggest that the plateau behavior in isotherms of adsorption at small concentrations is not corresponding to the monolayer coverage of the surface, but rather arises from a specific chemical interaction of aliphatic alcohols, alkanoic acids, and acetone with hydrated surface of silica gels. It is known, that the centers of adsorption on silica gels are the surface hydroxy groups which can be divided according to their IR absorption spectrum on isolated (narrow band of valent vibration frequencies 3740 - 3750 cm^{-1}), and bound ones which give a wide unstructured spectrum in the region of 3000 - 3700 cm^{-1}.[11] We think, that two plateaus character of adsorption isotherms is mainly due to differences in adsorption reactivities of these two types of hydroxy groups. It was shown that, during the adsorption of alcohols and acetone on the surface of silica gels, a decrease in absorption intensity in IR spectra of isolated and weakly bound hydroxy groups occurs (the corresponding frequencies of the last lay in the region close to the frequencies of isolated groups) (Figure 4). When the concentration is increased, the stronger bound hydroxy groups are taking part in adsorption, being "opened". For adsorbed acetone two bands of C=O valent

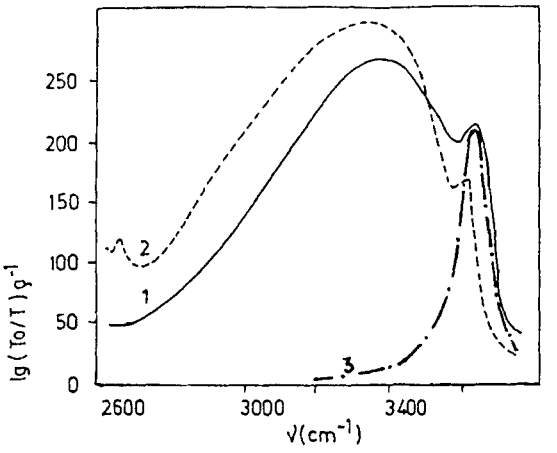

FIGURE 4 IR spectra for hydroxy groups of KSS-3 silica gel samples in solution of CCl_4 before (1), (3) and after (2) adsorption of CD_3OD. Samples (1) and (2) were calcinated at 120°C at atmospheric pressure, sample 3 - at 700°C for 3 hours at residue pressure of 10^{-4} torr. (Initial concentration of alcohol: $2.5*10^{-2}$ mol/l, 20°C, thickness of cell ρ = 0.5 mm, T_0 and T are intensities of incident and transmitted IR radiation).

vibrations were found (ν = 1695 cm^{-1} and ν = 1705 cm^{-1}), corresponding to the two forms of its adsorption (Figure 5). The first prevails at small and the second - at large concentrations of acetone. On partly dehydroxilated surface of SiO_2 (calcinated at 700°C) only one band of ν = 1705 cm^{-1} was found in IR spectrum of adsorbed acetone. The isotherm of adsorption on this surface was close to the Langmuir type, which points to the presence of one kind of adsorption centers only (Figure 2,b). These centers are likely to be the isolated OH-groups of silica surface (see spectrum (3) on Figure 4). The bound OH-groups had been removed during the dehydroxilation and the second plateau, which is due to the adsorption on these centers, was not present.

In the general case, the isotherms of adsorption of aliphatic alcohols, alkanoic acids, and acetone on the hyd-

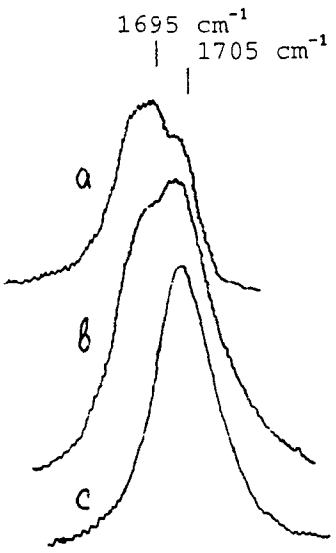

FIGURE 5 IR spectra for acetone adsorbed on KSS-3 silica gel samples: a) calcinated at 120°C, adsorption corresponds to the first plateau; b) calcinated at 120°C, adsorption corresponds to the second plateau; c) calcinated at 700°C, adsorption corresponds to the plateau.

rated surface of SiO_2 can not be considered as a superposition of two Langmuir isotherms, and their complex form can be described by introduction of a distribution of adsorption equilibrium constants.[6] This distribution can be wide enough to demand large adsorbate concentrations for monolayer coverage of the surface. The isotherms, obtained in the narrow range of concentrations, can lead to underestimate in the values of monolayer coverage and, as a result, to overestimation of D values.

Thus, the specific character of chemical interaction of adsorbate molecules with the surface of silica gels may lead to the dependence given in Eq.(1) with an effective fractal dimension D', value which depends on both the surface geometry and the mechanism of adsorption. The use of aliphatic alcohols, alkanoic acids, and kethones, as one

can see, needs a detailed analysis of adsorption isotherms in a wide range of concentrations. Some problems can also arise with the choice of cross-sectional areas of the yard-stick molecules. Although the methods of molecular dynamics can be applied to calculate the cross-sectional areas of organic molecules by simulating their possible conformations[8], it is still not completely clear how close are the equilibrium conformations of the molecules in the free and adsorbed state.

In relation to the factors mentioned above, we think, that development of a technique for measuring the fractal dimension D by adsorption of different aromatic molecules (benzene, naphthalene, anthracene, etc.) could be rewarding. These molecules do not contain functional groups and adsorption of these compounds exhibits normal character, that diminishes the role of chemical factor. Moreover, the cross-sectional areas of these rather rigid molecules are defined with a better accuracy. By studying adsorption of benzene on the surface of silica gels KSM-6 and KSS-3, we received the values of fractal dimension, close to the ones obtained from the upper plateaus of adsorption isotherms of alcohols and acids.

Steric factor

The steric factor of monolayer formation has another nature. It is related to the peculiarities of packing adsorbate molecules on the surface of micropores, if one takes into consideration the intrinsic volume of the molecules. Indeed, the adsorbed molecules occupy not only the place on the surface, but also the neighboring volume thus, creating steric difficulties for adsorption of the other molecules (the effect of "excluded volume").[12] As a result, the number of adsorbed volume molecules is always less, then the number of flat molecules of the same cross-sectional area. When volume yard-sticks are used in adsorption experiments, it results in underestimation of specific

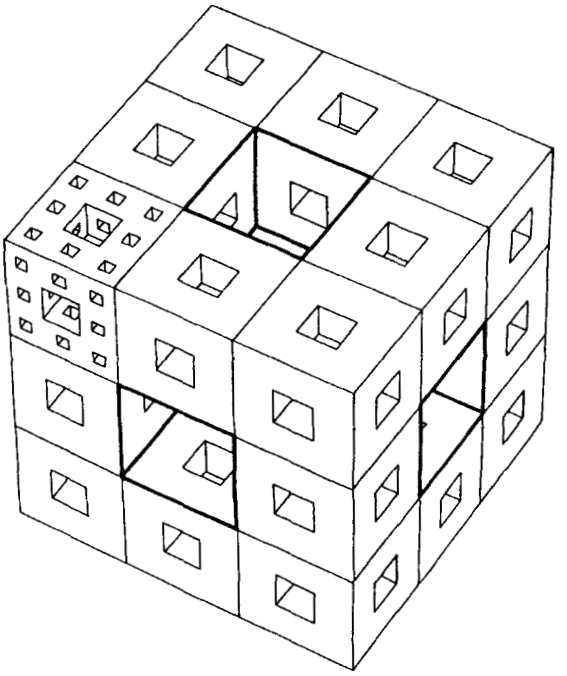

FIGURE 6 Menger sponge.

surface area. For example, to cover a single cubic pore of size r one needs 4 square "molecules" of cross-sectional area r^2, but only one cubic "molecule" of the same size and cross-sectional area. This effect is demonstrated here by simulation of adsorption of cubic "molecules" of different sizes on the surface of Menger sponge.

Menger sponge (Figure 6) is a fractal object, which is used to describe the structure of many catalysts and adsorbents.[4,13] Let us consider Menger sponge at iteration $k >> 1$. The minimum pore size of this sponge is $R_{min} = (1/3)^k$. The full surface area of this sponge S_0 is: $S_0 = 2\left((20/9)^k - (8/9)^k\right) \longrightarrow 2\,(20/9)^k$.[13]

Let us measure the surface area of this sponge by square yard-sticks of different size $R = R_{min} * (1/3)^n$, where n is digital. The result of our measurements will be the function:

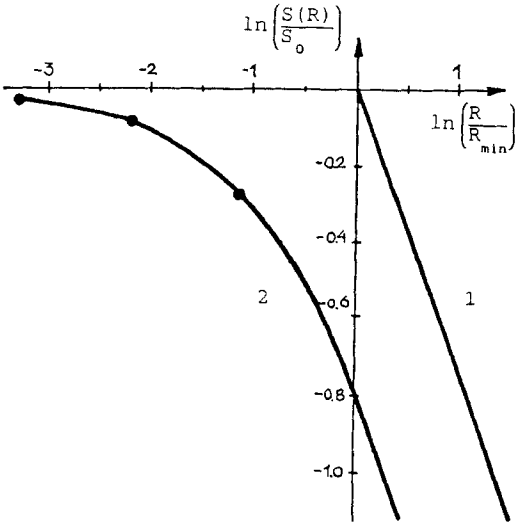

FIGURE 7 Measuring the surface of Menger sponge by sqaure (1) and cubic (2) yard-sticks of different sizes.

$$S(n) = \begin{cases} S_0 & \text{at } n > 0 \\ S_0 * (20/9)^n & \text{at } n < 0, \end{cases}$$

which gives us the law:

$$S(R) = \begin{cases} S_0 = \text{const} & \text{at } R < R_{min}, \\ S_0 * (R/R_{min})^{2-D} & \text{at } R > R_{min}. \end{cases} \quad (2)$$

The function (2) is a typical fractal law that describes the connection between the measured surface area and the size of yard-sticks used in the adsorption experiment. The law (2) predicts measuring the full surface area of adsorbent, when using adsorbate molecules of size $R < R_{min}$, and the values of surface area which are less than the true value, when using adsorbate molecules of size $R > R_{min}$. $D = \ln 20/\ln 3 = 2.72..$ is the surface fractal dimension of Menger sponge at $R_{min} < R < 1/3$. At the range of $R < R_{min}$ the surface of adsorbent is seen as flat and $D = 2$.

By using the volume yard-sticks of size $R < R_{min}$, the measured surface area, according to our calculations, is dependent on size R and always less than its true value S_0 (Figure 7), which is different from the case of flat molecules:

$$S_k(R) = \begin{cases} \frac{151}{340} S_0 (R/R_{min})^{2-D} & \text{at } R < R_{min}, \\ S_0 (1 - 12R/17R_{min}) & \text{at } R > R_{min}. \end{cases} \quad (3)$$

This is because the number of volume molecules which is necessary to cover the surface is always less than the number of flat molecules of the same cross-sectional area.

Thus, measuring the surface of Menger sponge by volume molecules, the result at $R < R_{min}$ is not connected with self-similarity of the surface, but with steric peculiarities of packing adsorbate molecules on the surface of narrow pores. If the variation of adsorbate size is small (usually in adsorption experiments the yard-stick sizes differ by a factor of 3-4), the experimental function (3) at $R < R_{min}$ can be approximated by equation (1), which will allow the calculation of the apparent fractal dimension D_a. Apparent fractal dimension D_a will show the relation between the size of pores R_{min}, which give the main impact to surface area, and the size of adsorbate molecules R:

$$D_a = \frac{d\ln S}{d\ln R} = 2 - \frac{d\ln(1 - 12R/17R_{min})}{d\ln R} =$$

$$= 2 + \frac{12R/17R_{min}}{1 - 12R/17R_{min}}. \quad (4)$$

Apparent fractal dimension D changes from $D = 2$ at $R \longrightarrow 0$ to $D_a = 2.72$ - the fractal dimension of Menger sponge - at $R = R_{min}$ (Figure 7).

One can also see that by using molecules of size $R > R_{min}$ both flat and volume, the measured surface area of Me-

nger sponge is described by the usual fractal law (2) with D-value equal to the surface fractal dimension of Menger sponge. However, when using the volume molecules, the values of the measured surface area are 340/151 ≈ 2.2 times less than those measured by flat molecules.

We think, that the result obtained for adsorption of cubic molecules can also be applied for adsorption of spherical molecules or close to spherical. In particular, it is shown in ref.[8] by means of conformation analysis, that the form of alkanoic acids and aliphatic alcohols can be described satisfactorily by ellipsoids with a relatively small ratio of axes (for example, 4.3 in the case of n-decanol). The form of iso-alcohols and acids was even closer to spheric. When adsorbing such non-flat molecules, the factors mentioned above may strongly influence the formation of monolayers.

Thus, the number of molecules of aliphatic alcohols, alkanoic acids or acetone adsorbed by silica is determined by both the geometrical structure of its surface and the thermodynamic characteristics of the interaction between adsorbate molecules and surface hydroxy groups. Both factors may lead to underestimation of specific surface area, when measured by adsorption techniques. Based on the analysis mentioned above, an accurate method for measuring monolayer adsorption and surface fractal dimension should be developed.

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