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## Abstract

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*PHYSICAL CHEMISTRY*

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# ADSORPTION FROM SOLUTIONS OF POLYDIMETHYLSILOXANE BY AEROSILS

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In a number of our works the influence of the chemical nature of the surface of adsorbents and fillers on the adsorption and adsorption energy of low-molecular-weight substances of different electronic and geometrical structure has been shown (see reviews ([1]-[3])). It is of interest to investigate the role of surface chemistry in the adsorption of high-molecular-weight substances, both nonpolar and possessing various functional groups. The present work gives the results of a study of adsorption from solutions of polydimethylsiloxane on three samples of highly dispersed nonporous silica—Aerosil—with different surface nature.

**Polymer.** The effective molecular weight of polydimethylsiloxane (PDMS) was about 350,000. Weighed portions of the polymer were dissolved in *n*-hexane and, to obtain a calibration curve, were analyzed in an ITR-2 interferometer cuvette 20 mm thick. The maximum polymer concentration in the solution was about 40 mg per 1 g of solution; moreover, dissolution of the polymer in preparing such a solution proceeded very slowly, through swelling. The maximum polymer concentration in *n*-hexane corresponded to a displacement of the interferometer compensator by 660 divisions. The accuracy of concentration determination was 0.2 mg/g.

**Filler samples.** Adsorption of PDMS was studied on three Aerosil samples with a specific surface area of 170 $m^2$/g. The initial Degussa sample was additionally subjected to hydration by heating on a water bath a suspension of Aerosil (up to 5% by weight) in acidified distilled water for 20 hr. This Aerosil was then repeatedly washed until chloride ions were removed and dried to constant weight at 250° in a drying oven (sample 1). Another portion of Aerosil, for the purpose of dehydrating the surface, was calcined at 800° to constant weight in air (sample 2). A third portion of Aerosil was treated with trimethylchlorosilane for 8 hr by boiling with a reflux condenser, then washed with acetone and evacuated in vacuum at 180° (sample 3). Analysis for the carbon content in sample 3 gave a value of 1.7%, which corresponded to coverage of the Aerosil surface by trimethylsilyl groups by approximately 70%.

**Fig. 1.** Calibration dependence of the displacement of the interferometer compensator scale divisions $i$ on the PDMS concentration in *n*-hexane.

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Figure 1: Fig. 1. Calibration dependence of the displacement of the interferometer compensator scale divisions $i$ on the PDMS concentration in $n$-hexane

Fig. 2

Figure 2: Fig. 2

Initial PDMS solutions with concentrations up to 40 mg/g of solution were prepared in separate vessels of 30 ml capacity. Then up to 0.3 g of filler and up to 5 ml of solution were introduced into the adsorption ampoule. Analyses of the equilibrium solution were carried out with an ITR-2 interferometer in a cuvette 20 mm thick ([4]). The calibration dependence of the interferometer readings on the weight concentration of the prepared polymer solutions is presented in Fig. 1 (see ([5])). The rate of dissolution of the polymer depends on concentration;

complete dissolution of the polymer to a concentration of 20-30 mg/g was achieved in several tens of hours. The ampoules containing the adsorbent and the polymer solution were shaken for several days, although equilibrium was practically reached in two hours. The value of Gibbs adsorption was calculated by formula (1)

$$x^{(g)} = \frac{\gamma_0 - \gamma}{m} \cdot g \tag{1}$$

where $\gamma_0$ and $\gamma$ are the initial and equilibrium concentrations of the polymer in $n$-hexane, $g$ is the total weight of the solution, and $m$ is the weight of the adsorbent. At such low concentrations in solution, the value of Gibbs adsorption practically does not differ from the total content of polymer on the surface of the adsorbent.

**Results and discussion.** Figure 2 gives the adsorption isotherms of PDMS on the investigated aerosil samples. In all cases the isotherms rise steeply, and the adsorption practically reaches a limit already at low concentrations. Additional dehydration of the surface

**Fig. 2.** Adsorption isotherms of PDMS by aerosils: **1**—dried at 250°, **2**—calcined at 800°, **3**—modified by reaction with trimethylchlorosilane, and **4**—molecular sieve 13X

**Fig. 3.** Isotherms of the adsorption values of PDMS per unit surface of aerosil (**1**), glass (**2**) and an iron oxide film (**3**). Isotherm **4** is recalculated

Fig. 3

Figure 3: Fig. 3

from isotherms (**2, 3**) for molecular weight 350,000

of aerosil at 800° changes the adsorption of PDMS almost not at all. This is in agreement with the fact that dehydration of the silica surface has almost no effect on the adsorption energy of nonpolar molecules that do not possess large quadrupole moments or $\pi$-bonds ($^{1-3,6,7}$). Treatment of aerosil with trimethylchlorosilane, i.e., grafting trimethylsilyl groups onto its surface, reduces the adsorption of PDMS by almost a factor of two. Similar treatment of aerosil also causes a sharp decrease in the adsorption and heats of adsorption of vapors of saturated hydrocarbons, in particular *n*-hexane ($^{8-10}$). The decrease in PDMS adsorption upon treatment with trimethylchlorosilane can be explained, as for low-molecular substances ($^{8-10}$), by a decrease in the dispersion interaction of the polymer molecules with the silica itself as a result of moving the adsorbing molecules away from it by the thickness of the layer of trimethylsilyl groups, which have only weak attraction energy. This interlayer of trimethylsilyl groups prevents close contact of the adsorbed molecules directly with the atoms forming the surface of the silica itself.

Perkel and Ullman ($^{11}$) investigated the adsorption of PDMS on iron spheres with a specific surface area $s = 0.67$ m$^2$/g (by BET) and on Pyrex glass powder with $s = 2.01$ m$^2$/g from various solvents (hydrocarbons, carbon tetrachloride, acetonitrile, and others). They showed that adsorption, expressed in mg per 1 g of adsorbent, increases with increasing molecular weight of the polymer (from 26,000 to 536,000). The use of moistened solvents lowers the adsorption of the polymer owing to displacement of the polymer molecules by water molecules, which are capable of forming hydrogen bonds with the hydroxyl groups of oxide surfaces. The adsorption of PDMS also decreased when benzene and especially aceto-

nitrile as a result of strong adsorption of these solvents themselves (capable of specific interaction with the hydroxyl groups of the surface) on the hydrated surface of glass and on the iron oxide film.

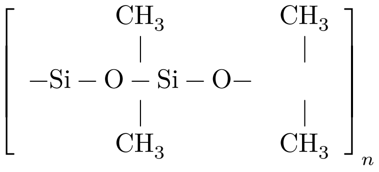
Figure 3 gives isotherms, referred to unit surface area of the adsorbents, for the adsorption of PDMS at 20° on glass and iron powders (calculated by us from the data of (11)) and on the initial Aerosil (our data, see Fig. 2). The first two isotherms refer to the adsorption of PDMS with a molecular weight of 536,000 in the region of low equilibrium concentrations of PDMS in *n*-hexane. From Fig. 3 it is seen that in all cases the values of PDMS adsorption per unit surface area are of the same order; moreover, for PDMS of the same molecular weight on glass and on an iron oxide film they are very close. The maximum value of PDMS adsorption (mol. wt. 536,000) on glass is 1.6 mg/m$^2$; the adsorption of PDMS (mol. wt. 350,000) on Aerosil is 0.7 mg/m$^2$. Perkel and Ullman (11) obtained, in bilogarithmic coordinates, a linear dependence of the maximum adsorption of PDMS attained in their experiments on molecular weight. From this dependence the maximum adsorption of PDMS with mol. wt. 350,000 on glass is found to be 1.2 mg/m$^2$. This value is still closer to the value found by us, 0.7 mg/m$^2$, for the maximum adsorption of PDMS (mol. wt. 350,000) on Aerosil. Complete agreement is difficult to expect, since the geometry of the nonuniform surface of Aerosil and glass affects differently the adsorption of PDMS macromolecules and the adsorption of small nitrogen molecules used to determine the specific surface area by the BET method (12). Thus, the values of PDMS adsorption from solutions in saturated hydrocarbons (*n*-hexane and *n*-heptane) per unit surface area of Aerosil and glass are rather close.

If the adsorption value is calculated as the number of molecules per unit surface area of the adsorbent, $\alpha$, assuming that all PDMS macromolecules have the same molecular weight (536,000 and 350,000), then we obtain: at an equilibrium concentration of 1 mg/g, $\alpha = 1800$ for glass and $\alpha = 1400$ molecules/$\mu^2$ for Aerosil. These adsorption values correspond to areas per macromolecule, $\omega = 1/\alpha$, of about 50,000 $\text{Å}^2$ for glass and 60,000 $\text{Å}^2$ for highly dispersed Aerosil. It is of interest to compare these values with $S_p$, the surface of one effective Aerosil particle, whose diameter can be calculated by assuming a spherical shape for it and a density close to that of quartz glass (2.2 g/cm$^3$). In this case

$$D = \frac{6 \cdot 10^4}{2.2 \cdot 170} = 160\ \text{Å} \quad \text{and} \quad S_p = 4\pi D^2 = 80\,000\ \text{Å}^2.$$

This value is rather close to the area per one PDMS macromolecule. Thus it is possible that, at maximum adsorption, one Aerosil particle of this dispersity is enveloped approximately by one PDMS macromolecule.

Concepts of the structure of solutions of high-molecular compounds lead, in the main, to two types of macromolecular state: globular (coiled into balls) and fibrillar (fibrous) (13). Like polyethylene, PDMS is usually classed as a linear macromolecule of the type (11):

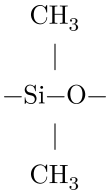


$$\left[\begin{array}{ccccccc} & & & \mathrm{CH_3} & & & \mathrm{CH_3} \\ & & & | & & & | \\ -\mathrm{Si} & - & \mathrm{O} & - & \mathrm{Si} & - \mathrm{O}- & \\ & & & | & & & | \\ & & & \mathrm{CH_3} & & & \mathrm{CH_3} \end{array}\right]_n$$

It is considered that such linear macromolecules in solution, under the action of intramolecular forces, are in a coiled state (in the form of spirals); thus the interaction of macromolecules with one another and with the surface of solids is effected through contacts only with individual segments of such a spiral (13-15).

The data given above rather indicate an uncoiling of such a spiral in the field of adsorption forces, with the formation on the adsorbent surface of a layer of fairly densely packed macromolecules. An estimate of the thickness of the ad-

of the sorbed layer, $\tau = v_m/\omega$, where $v_m = 640\,000\ \text{Å}^3$ is the volume of one PDMS macromolecule (assuming that the density is 0.9 g/cm$^3$, the molecular weight is 350,000, and the polymer consists of macromolecules of a single molecular weight), and $\omega = 60\,000$ Å$^2$ is the area falling on average to one macromolecule, gives $\tau$ of about 10 Å. This thickness of the adsorbed layer is close to the thickness of an extended PDMS molecule, for which calculation from the van der Waals model gives 7 Å. Calculation from the adsorption data of the area falling on one unit



$$-\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{\overset{|}{\underset{|}{Si}}}}-O-$$

gives $\omega' = 74\omega/M = 13$ Å$^2$, which is also fairly close to the possible van der Waals area of the unit under dense packing. Thus, in the field of the adsorption forces of the filler, these macromolecules probably straighten and form a sufficiently dense monomolecular layer.

We also studied the adsorption of PDMS from solutions in *n*-hexane by a granulated 13X molecular sieve, preliminarily calcined at 600°. The dimensions of the windows into most of the channels of the porous crystals of this zeolite are only about 10 Å [16]. It is seen from Fig. 1 that the adsorption of PDMS by zeolite 13X is almost five times less than by the original aerosil, which approximately corresponds to adsorption on the outer surface of the zeolite crystals and on the surface of the large pores connecting them in the tablets. Although, by their dimensions, PDMS macromolecules could penetrate into the zeolite channels, they first envelop the outer surface of the zeolite and can no longer diffuse into the narrow channels of its crystals.

Thus, it is possible that PDMS macromolecules, in the field of the adsorbent, envelop its particles with a layer of approximately monomolecular thickness. This conclusion should subsequently be tested on different systems by different methods.

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