

ADSORPTION OF ORGANICS ON THERMALLY TREATED SOLIDS OBTAINED FROM COLLOIDAL SILICA

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Adsorption isotherms of three adsorbates on the solid beads obtained from colloidal silica were determined by means of gas chromatography at low surface coverages, when lateral interactions between the adsorbed molecules are negligible. The influence of thermal pretreatment on the adsorption properties of the solids was investigated in the temperature range from 343 to 423 K, while the solids were heated between 523 K and 1 223 K. The thermodynamic parameters of adsorption have been determined and used to discuss the adsorbate-adsorbent interactions.

Among a few common adsorbents in gas-solid chromatography (GSC), silica is the one most frequently used. This material is of particular value for separation of gases and low boiling organic compounds. Its large disadvantage is the surface heterogeneity, reflecting in peak asymmetry, and the retention times being dependent on sample size. Hence, either thermal or chemical treatment or their combinations, is often applied to the SiO₂ in order to eliminate the highly active sites on the surface, to decrease overall retention, and to enhance peak symmetry.

An extensive GC study on various silica samples has been undertaken in late sixties¹⁻⁵, on the near-to-zero surface coverages. In order to avoid surface heterogeneity, various treatments such as modification with inorganic agents including acid/base washing or soaking into the various inorganic salts, modification with organic materials — mostly polymers in a monolayer form, and finally, thermal treatment have been applied. Sawyer and coworkers^{6,7} have modified Porasil type silica with various inorganic salts. As studied by Baigupkeova *et al.*⁸ small amounts of Al₂O₃ added to the silica matrix enhanced specific interaction between aromatics and ethers with surface resulting in longer retentions and more tailed peaks. The effect was considered as an "increasing of specific adsorption". Aue and colleagues⁹ showed an excellent separation of alcohols using solid samples pretreated with a thermal/polymeric action. Various bases and salts have been used as silica modifiers by Bebris and coworkers¹⁰, Barry and Cooke^{11,12}, and Datar and Ramanathan¹³, who showed that the salt loading introduces a significant decrease in retention times. Changes caused by an reaction of silica gel with alcohol are very efficient in specific surface reduction¹⁴, reflecting in retention times shortening¹⁵. Most often, waxes, such as Carbowax 20 M, are used as chemical alternators, while Kiselev and coworkers¹⁶ reported a polyamide as an organic modifier.

The influence of thermal modification on separation and adsorption abilities of the silica packings used in high performance liquid chromatography (HPLC), GLC, and GSC were studied by Scott and Kučera^{17,18} and Smolková *et al.*^{19,20}. Recently Milonjić and Kopečnik²¹ showed that the thermal treatment of SiO₂ samples obtained from colloidal silica significantly changed the adsorption properties of the solids. The role of thermal and hydrothermal treatment of Porasils on adsorption isotherms of benzene, n-hexane, and cyclohexane was studied by Smolková and Feltl²².

In the first two papers of our series of study, we investigated the thermodynamics of adsorption on the silica beads obtained from colloidal material with surface properties altered by the ion exchange procedure²³ and by the thermal treatment²¹, at near-to-zero coverage conditions (Henry law region), and the thermodynamic functions of adsorption were determined by the adsorbate-adsorbent potential energy functions.

The aim of this paper is to extend previous measurements to a higher surface coverage and, hence, to more complicated interactions on the surface. Also, the study of the thermal treatment role was envisaged as one of the goals of the work.

EXPERIMENTAL

Colloidal silica was obtained from liquid glass by an ion-exchange method²⁴ described previously. The solid material was prepared by coagulation of colloidal silica containing uniform particles, 9 nm in diameter. Coagulation was carried out with NaCl, followed by immediate filtration. The solid phase was then transferred to a polyethylene bottle containing 200 ml of 0.15 mol l⁻¹ HCl, and allowed to equilibrate for 24 hours. The washing procedure was repeated, and the pH of solution after equilibration was 2.2 corresponding to the pH at the point of zero charge of fully protonated silica. The solid phase was separated by filtration, dried in air, and washed with double distilled water until no further reaction with chloride ions was observed. The material was then dried in an air oven at 383 K for 24 hours. Dried material was crushed and sieved, 0.210–0.315 mm fraction was used as initial packing and for further thermal treatments. Six different temperatures were applied to the starting material: 423, 523, 773, 1 073, 1 223, and 1 373 K, respectively. First two treatments were of an "in column" type, carried out in a stream of nitrogen overnight. Other modifications were performed in a muffle furnace, air atmosphere for the period of four hours. Water contents of these silica samples at the given treatment temperatures were estimated from the sample-mass loss after annealing. They are as follows: 0.25, 0.85, 2.45, 4.75, 6.15, and 7.00 mass % for 423, 523, 773, 1 073, 1 223, and 1 373 K, respectively.

Specific surface areas of the obtained materials were determined by a Ströhlein area meter using the single point nitrogen adsorption method. The values found for the first five thermally modified materials are 275 ± 17, 259 ± 3, 262 ± 28, 248 ± 16, and 152 ± 5 m² g⁻¹, respectively. For the solid heated at 1 373 K, the specific surface area was 3 m² g⁻¹. The change of the silica specific surface area with the applied thermal treatment temperature has been discussed at length in the previous article²¹.

The X-ray patterns of the silica samples were obtained using a Siemens Kristalloflex 4 instrument with CuK_α radiation. The X-ray diffraction patterns revealed that the amorphous structure of all the samples remains unchanged upon heating²¹.

Adsorption experiments were performed on a laboratory modified Perkin-Elmer gas chromatograph model 881 equipped with a HWD detector and modified to a single column system, with

a mercury manometer for measuring inlet pressure, p_i . Outlet pressure, p_o , was assumed to be equal to the atmospheric pressure which was measured by a precision barometer. The column temperature was measured by a mercury thermometer situated inside the hole drilled through the gas chromatograph thermostat wall. The precision and accuracy of such an experimental set-up were checked up by measuring the partition coefficients, K_S , of several organics (n-hexane, n-heptane, cyclohexane, benzene, chloroform, and dichloromethane) on squalane. The obtained K_S values were equal to the generally accepted literature data within $\pm 2\%$, with the exception of chloroform for which the deviation from tabulated data reached as much as -5% (ref.²⁵).

Stainless steel 2 m long, 2.2 mm i.d. columns were packed with thermally treated silicas. The mass of the column packings ranged from 3.26 to 3.48 g. Dry nitrogen was used as a carrier, while the gas chromatographic experiments were performed at 323, 343, 363, 393, and 423 K.

Three adsorbates were selected each representing a class of organics, *i.e.*, n-hexane, cyclohexane, and carbon tetrachloride for aliphatics, alicyclics, and halogen derivatives, respectively. They were obtained from various sources, used "as received" and introduced into the chromatograph by means of 1 μ l Hamilton microsyringe. All the measurements were made in triplicate at each temperature. Isotherms were constructed from at least eight injections of different volumes of liquid adsorbate. HWD was checked for linearity, while graphical integration was applied to the chromatographic peaks obtained.

RESULTS AND DISCUSSION

The specific surface area of the silica samples used remained practically unchanged by heat treatment up to 1 073 K and, after that temperature, a sharp decrease in S_a was observed. Due to the low S_a value of the material treated at 1 373 K it was omitted from the gas chromatographic experiments.

To get the adsorption isotherms, the Elution by Characteristic Point (ECP) technique, introduced by Cremer and Huber²⁶ and detailed by Kiselev and Yashin²⁷, was used throughout the paper. Assuming that the recorded peak height, h , is proportional to the adsorbate partial pressure, p , the detector could be then calibrated by injecting a known volume, V , of the adsorbate. Under these conditions the dependence of p on the peak height can be written²⁷ as follows:

$$p = \frac{VxRT}{V_m S f} h. \quad (1)$$

Here, x is the chart speed, V_m is the adsorbate molar volume, S stands for the peak area, and f denotes the volumetric flow rate at column temperature T . R is the gas constant.

The adsorption isotherm is obtained by integrating Eq. (2), namely,

$$a = \frac{1}{RTw} \int_0^p V_N dp. \quad (2)$$

In the above equation a is the surface concentration of the adsorbate given in mole per gram, w denotes the weight of adsorbent in the column under investigation, while V_N is the net retention volume corresponding to partial pressure p , corrected for pressure drop across the column by the James–Martin compressibility factor, j , given as

$$j = \frac{3}{2} \left[\frac{(p_i/p_o)^2 - 1}{(p_i/p_o)^3 - 1} \right]. \quad (3)$$

In connection with this, it should be noted that Conder and Purnell^{28–30} have derived equations analogous to Eqs (1) and (2) which, besides the j corrections, take into account the sorption effect and gas phase imperfection as well. These two corrections are trivial, if the mole fraction of the adsorbate in the gas phase is kept small³¹, as it is the case in this work, and therefore, they were neglected in our calculations.

A typical set of chromatographic traces is shown in Fig. 1. Common to all the peaks is an excellent coincidence of the rear parts of the asymmetrical bands. This means that the equilibria at all partial pressures were indeed reached. Further, the front boundaries are practically vertical within close to the base line, implying that the kinetic effects are negligible. For the systems studied, retention volume corresponding to the peak maximum increases with injection size.

Application of Eqs (1) and (2) to these envelopes allows the calculation of a smooth isotherm and the procedure has been described in details in the classical work²⁷ devoted to this problem.

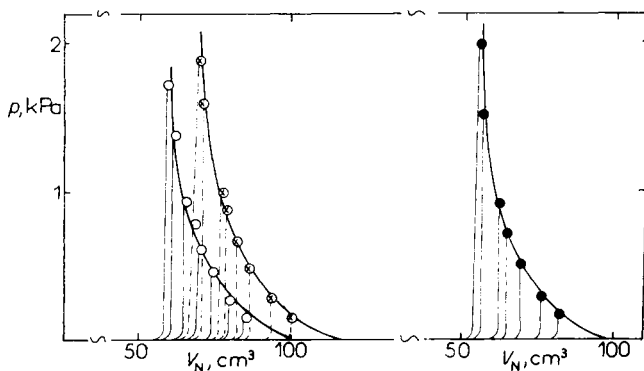


FIG. 1

Chromatographic peak shapes for larger injections of adsorbates on silica thermally modified at 773 K. Experimental temperature 393 K. Injection sizes 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.8, and 1.0 μ l. The points indicate peak maxima; \circ n-hexane, \otimes carbon tetrachloride, \bullet cyclohexane

Figs 2 and 3 present the examples of the computed isotherms for the adsorbates on silica thermally treated at 773 K. The similar patterns were obtained for other samples and other gas chromatograph temperatures. Characteristic to all is a near-to-linear dependence of a vs p with slight concavity toward partial pressure axis. This appearance is characteristic for the initial portion of the adsorption isotherm, having the most pronounced adsorbate-adsorbent interaction.

Experimental adsorption isotherms could be formally fitted by the Freundlich or Langmuir type equation³². The Freundlich isotherm is expressed as

$$a = kp^{1/n}, \quad (4)$$

where k and n are the constants dependent on each adsorbate-adsorbent pair and experimental temperature. Somewhat poorer fit to our experimental data is obtained using the Langmuir isotherm

$$a = a_m \frac{n'p}{1 + n'p}. \quad (5)$$

In the latter equation, a_m is the sorbed amount corresponding to the monolayer coverage, and n' is the constant.

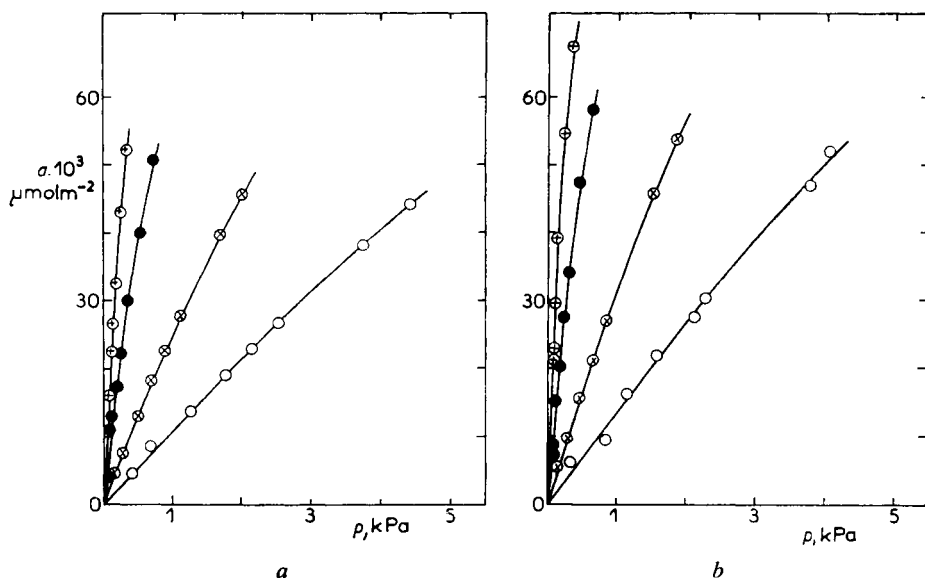


FIG. 2

Adsorption isotherms for *a* cyclohexane, *b* carbon tetrachloride on silica thermally treated at 773 K. Points: experimental results at ○ 423, ⊙ 393, ● 363, ⊕ 343 K. Solid lines: Freundlich fits

Examples of the fitting procedure are presented in Figs 2 and 3, while the Freundlich k and n constants for all the experimental isotherms are compiled in Table I. Inspection of Table I shows that the n values are never far from unity, an expected matter, since all the isotherms are never too far from linearity.

It is worth noting some interesting features of the Freundlich isotherm constants behaviour under the present experimental conditions. For the fixed experimental temperature and given adsorbate the Freundlich k value when plotted against thermal treatment temperature, exhibits a parabolic dependence that reaches maximum in the region between 773 and 1 073 K. This is valid, with no exception, for all adsorbates used, and some examples are given in Fig. 4. It should be pointed out that this region coincides with the thermal treatment temperature interval in which the solid surface exhibits maximum of sorption activity²¹. When $\ln k$ is plotted vs

TABLE I

Constants of Freundlich isotherms (k in $\text{mmol m}^{-2} \text{Pa}^{-2}$) for adsorbates with different thermally treated silicas. T_1 , thermal treatment temperature, T_c , column temperature

T_1 K	T_c K	n-Hexane		Cyclohexane		Carbon tetrachloride	
		$10^5 k$	n	$10^5 k$	n	$10^5 k$	n
423	423	1.12	1.056	1.12	1.057	1.46	1.051
	393	3.25	1.081	3.42	1.101	3.34	1.035
	363	13.8	1.146	13.7	1.173	19.3	1.166
	343	47.9	1.249	43.9	1.280	68.1	1.294
523	423	1.39	1.056	1.40	1.057	1.77	1.048
	393	4.14	1.091	4.12	1.104	5.38	1.083
	363	16.8	1.153	14.6	1.148	22.3	1.161
	343	56.5	1.274	37.6	1.202	74.8	1.295
773	423	1.79	1.075	1.94	1.084	2.83	1.112
	393	4.29	1.076	4.80	1.104	6.08	1.107
	363	23.2	1.190	23.8	1.216	25.6	1.182
	343	69.5	1.277	61.2	1.293	79.5	1.298
1 073	423	1.84	1.091	1.93	1.088	1.50	1.055
	393	5.19	1.119	5.60	1.133	4.48	1.099
	363	18.3	1.181	19.5	1.203	14.3	1.147
	343	51.8	1.239	52.2	1.272	38.6	1.204
1 223	423	0.95	1.024	1.17	1.040	0.90	1.006
	393	2.26	1.037	2.64	1.054	1.48	0.982
	363	7.28	1.070	7.12	1.070	6.41	1.062
	343	8.48	0.938	15.3	1.082	14.9	1.100
	323	51.1	1.158	50.7	1.187	37.3	1.122

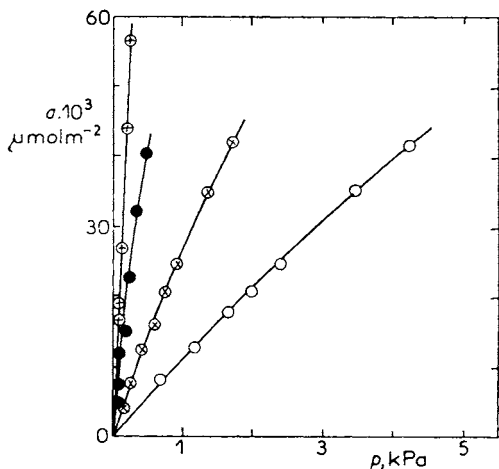


FIG. 3

Adsorption isotherms of n-hexane on silica thermally treated at 773 K. Points: experimental results labeling as in Fig. 2, solid lines: Freundlich fit

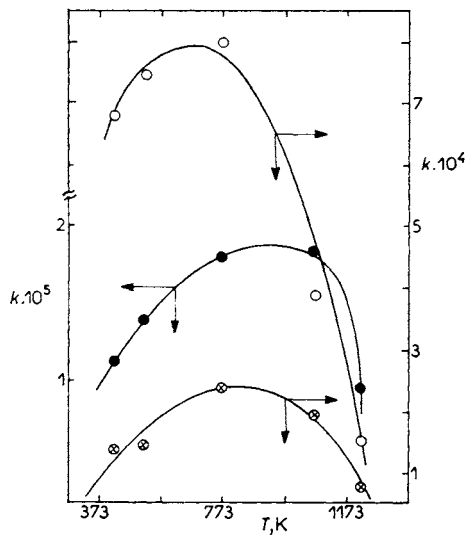


FIG. 4

Dependence of the Freundlich k constant on thermal treatment temperature; ● n-hexane at 423 K; ○ carbon tetrachloride at 343 K, ⊙ cyclohexane at 363 K

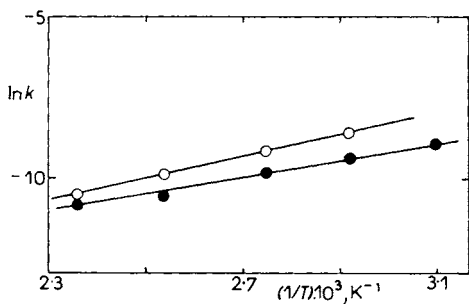


FIG. 5

Dependence of $\ln k$ vs $1/T$ for carbon tetrachloride on various thermally treated silicas: ○ at 523 K, ● at 1223 K

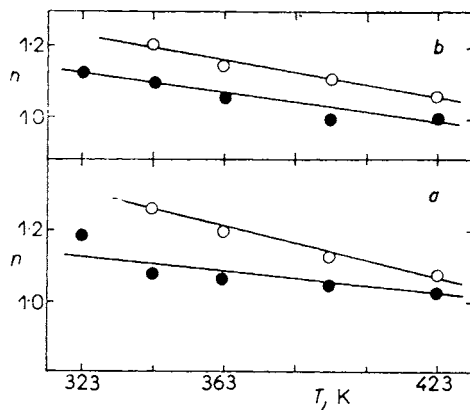


FIG. 6

Dependence of the Freundlich constant n on column temperature for silica treated at 1073 K (open circle) and at 1223 K (filled circle), a cyclohexane, b carbon tetrachloride

inverse experimental temperature (Fig. 5), a set of separate straight lines could be drawn. Each one corresponds to the particular thermal treatment temperature. Their sequence follows the thermal treatment temperature in analogous way as in Fig. 4. Consequently, the upper line in Fig. 5 corresponds to the material treated at 773 K, while the lower one is for silica treated at 1 223 K. Similarly, the dependences for other thermal treatment temperatures are all linear.

A link between the constant n and the column temperature is shown in Fig. 6. Quite alike to the Fig. 5, a set of linear dependences is present, the lower being constructed from the points belonging to the highest SiO_2 thermal treatment temperature. Here, we note that the thermal treatment at 1 223 K gives, as a result, the sample with a considerably reduced specific surface area, and a significant loss of silanol groups, *i.e.*, some increase of amount of siloxane groups²¹ on the surface.

The partition coefficient of an adsorbate at zero coverage can be deduced from the initial slope of the adsorption isotherm using the relationship

$$K_S = \left[\frac{aRT}{p} \right]_{a \rightarrow 0} \quad (6)$$

Table II lists the K_S values calculated from the initial (linear) part of adsorption isotherm by least square treatment applied to Eq. (6) for all the studied adsorbates at 393 K. This temperature was selected to enable a direct comparison between the calculated data and the K_S values experimentally obtained from the zero coverage measurements on the thermally treated silicas²¹. The slope analysis permits evaluation of the standard deviation in K_S , and these are included in Table II.

TABLE II

Partition coefficients, K_S (ml/m^2), of adsorbates on silicas thermally treated at various temperatures, obtained from zero coverage measurements (ref.²¹), and from Eq. (6). The column temperature 393 K. T_1 temperature of thermal treatment

T_1 K	n-Hexane		Cyclohexane		Carbon tetrachloride	
	K_S ref. ²¹	K_S Eq. (6)	K_S ref. ²¹	K_S Eq. (6)	K_S ref. ²¹	K_S Eq. (6)
423	0.093	0.086 ± 0.006	0.092	0.078 ± 0.006	0.131	0.153 ± 0.026
523	0.111	0.100 ± 0.011	0.108	0.091 ± 0.009	0.157	0.139 ± 0.012
773	0.130	0.116 ± 0.007	0.126	0.117 ± 0.006	0.172	0.126 ± 0.003
1 073	0.132	0.110 ± 0.010	0.136	0.102 ± 0.010	0.134	0.135 ± 0.015
1 223	0.078	0.076 ± 0.009	0.080	0.074 ± 0.006	0.078	0.077 ± 0.004

Under condition of finite surface coverage, the application of the Clausius–Clapeyron equation to the adsorption isotherm at different experimental temperatures permits the calculation of the isosteric heat of adsorption, q_{st} (refs^{33,34})

$$\left[\frac{\partial(\ln p)}{\partial(1/T)} \right]_a = - \frac{q_{st}}{R} \quad (7)$$

The following procedure was adopted throughout this work. Experimental data were fitted using the Freundlich constants cumulated in Table I, and from such smoothed isotherms, p values were obtained for the constant surface coverage, a . The values of q_{st} for various coverages for the three adsorbates were determined between 343 and 413 K. Fig. 7 shows the plots of q_{st} against the surface coverage for carbon tetrachloride. Those for n-hexane and cyclohexane are similar to that mentioned above. At this point, it is interesting to see that the values, $-\Delta H_d$, for the standard differential enthalpies of adsorption of the studied adsorbates for zero coverage conditions²¹ and q_{st} values are interrelated, to a good approximation, by the equation

$$q_{st} = -\Delta H_d + RT, \quad (8)$$

where T stands for the mid-temperature of the temperature interval studied. In Fig. 7, filled triangles are used to label the q_{st} values calculated from the published data²¹, and Eq. (8). The values so obtained are equal to the q_{st} values at zero coverage. Bearing in mind that the least square treatment of Eq. (7) gives an average q_{st} error of $\pm 3\%$, i.e., roughly $\pm 1.5 \text{ kJ mol}^{-1}$, the agreement between the two measurements is very good, and it holds for all the systems under investigation.

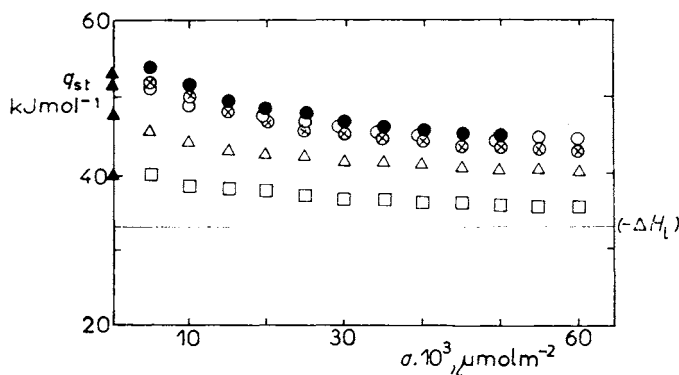


FIG. 7

Dependence of the isosteric heats of adsorption, q_{st} , of carbon tetrachloride on silica surface coverage for various thermally treated silicas: ● at 423 K; ⊗ at 523 K; ○ at 773 K; △ at 1 073 K; and □ at 1 223 K. ▲ values calculated using Eq. (8) and data reported in ref.²¹

It can be seen from Fig. 7 that q_{st} decreases with increasing thermal treatment temperature, approaching the value for the enthalpy of liquefaction, $-\Delta H_1$, at higher loadings.

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