Thermodynamic characteristics of hydrocarbon and chloroalkane adsorption by polymethylsilsesquioxane

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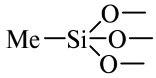
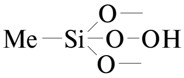
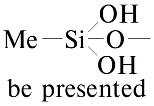
Adsorption of *n*-alkanes (C_7H_{16}—$C_{11}H_{24}$), cyclohexane, benzene, $CHCl_3$, CCl_4, and $ClCH_2CH_2Cl$ by polymethylsilsesquioxane $[MeSi(OH)_{0.4}O_{1.3}]_n$ was investigated by inverse gas chromatography in the Henry region. The adsorption isotherms are linear for all adsorbates. The standard changes in the thermodynamic parameters of adsorption were determined. The absence of specific selectivity with respect to aliphatic, cyclic, or aromatic hydrocarbons or chloroalkanes indicates that the adsorbent is chemically homogeneous.

Key words: polymethylsilsesquioxane, adsorption, hydrocarbons, chloroalkanes, adsorption isotherms, adsorption energy, adsorption entropy.

Sorbents based on polyorganylsilsesquioxanes $[RSi(OH)_mO_{1.5-0.5m}]_n$ are widely used in adsorption, catalysis, and chromatography, as well as for removal of toxicants from the organism.[1—4] In these processes important roles are played by not only the pore size and specific surface of an adsorbent, but also its chemical composition: the nature of the organic substituent R and the presence of silanol (—Si—OH) and disiloxane (—Si—O—Si—) groups. The study of the properties of the adsorbent surface and intermolecular interaction of the surface groups with various organic substances makes it possible to perform a target search for new adsorbents and modification of known adsorbents to expand their further practical application.

Adsorption of *n*-alkanes (C_7H_{16}—$C_{11}H_{22}$), *cyclo*-C_6H_{12}, C_6H_6, $CHCl_3$, CCl_4, and $ClCH_2CH_2Cl$ on cross-liked partially hydrated polymethylsilsesquioxane (PMSS) in the Henry region was studied by inverse gas chromatography. This sorbent consists of the  $Me{-}Si(O{-})_3$ and  $Me{-}Si(O{-})_2{-}O{-}OH$ fragments and an insignificant amount of the  $Me{-}Si(OH)_2{-}O{-}$ fragment. Its chemical composition can be presented by the formula $[MeSi(OH)_{0.4}O_{1.3}]_n$.

Experimental

Synthesis of polymethylsilsesquioxane. A solution of methylchlorosilane (50 g) in diethyl ether (100 g) was placed in a round-bottom three-necked 1-L flask equipped with a reflux condenser and a dropping funnel. Water (200 mL) was added for 1.5—2 h to the stirred solution cooled to 5 °C. Then the obtained mixture was heated to 50—60 °C (water bath) and stirred for 2—3 h. Solid polymer that formed was separated, washed with water until a negative reaction to Cl^- was achieved, and dried first in the air and then at 200 °C for 16—17 h to constant weight. PMSS was obtained in 85.7% yield (20.2 g). Found (%): Si, 40.01; C, 18.22; H, 5.05. $SiMe_{3.4}O_{1.7}$. Calculated (%): Si, 39.66; C, 15.79; H, 4.82. IR, ν/cm^{-1}: 2920 (C—H); 1410 (Me); 1120, 1020 (Si—O—Si); 784 (Si—C); 416 (Si—O—Si). The particle size of PMSS was 0.1—0.2 mm, its specific density was 0.52 g cm^{-3}, and the total pore volume was 0.285 cm^3 g^{-1}. The specific surface S_{sp} determined by gas chromatography[5] (silica gel L with a specific surface of 750 m^2 g^{-1} was used as a standard) was equal to 895 m^2 g^{-1}.

Adsorption was studied at 135—185 °C using a Chrom-5 chromatograph (heat capacity detector, carrier gas helium). Chromatographically pure substances served as sorbates and were used as received. The adsorption isotherms calculated by the known formulas[6] are linear for all adsorbates (Fig. 1). The

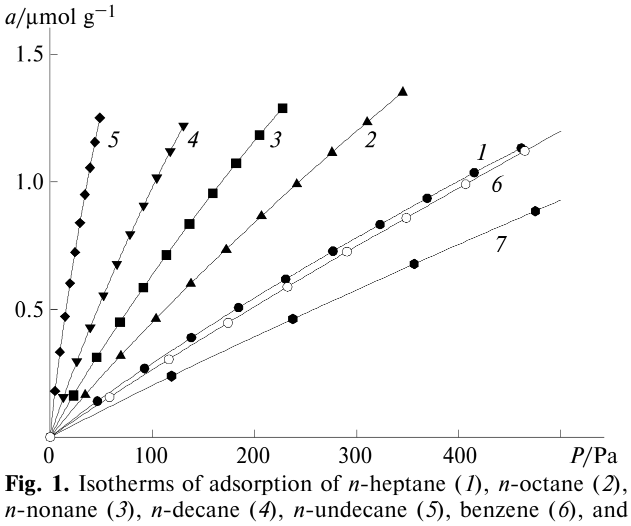


Fig. 1. Isotherms of adsorption of *n*-heptane (*1*), *n*-octane (*2*), *n*-nonane (*3*), *n*-decane (*4*), *n*-undecane (*5*), benzene (*6*), and chloroform (*7*) by polymethylsilsesquioxane at 185 °C.

Published in Russian in *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 12, pp. 2033—2036, December, 2000.

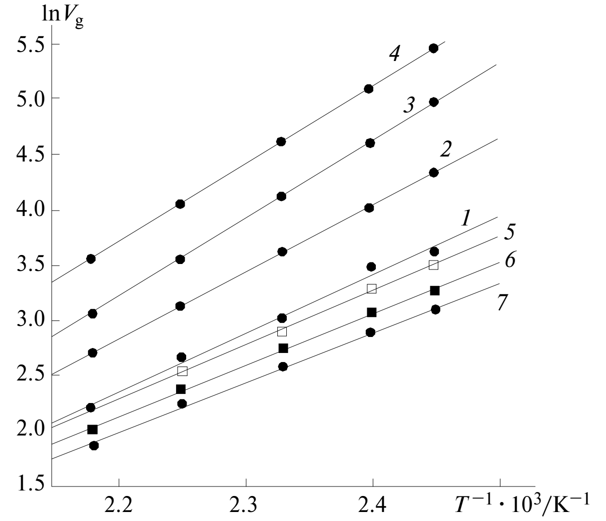


Fig. 2. The plots of the logarithms of limiting retention volumes of the adsorbates (V_g) *vs.* inverse temperature for *n*-heptane (*1*), *n*-octane (*2*), *n*-nonane (*3*), *n*-decane (*4*), benzene (*5*), 1,2-dichloroethane (*6*), and chloroform (*7*).

exception is undecane, which exhibits nonlinear isotherms at temperatures below 156 °C. Thus, at elevated temperatures and low doses of the adsorbate, the adsorption isotherms obey Henry's law, and for the constant of adsorption equilibrium, $K_1(a,p)$, that is independent of the coverage of the adsorbent surface, we can write $K_1(a,p) = V_g/RT$. This allows us to use the temperature plots of the specific retention volumes of adsorbates V_g (Fig. 2) to calculate the isosteric enthalpies of adsorption at zero coverage, ΔH°_{ads}.

The standard change in the molar free Gibbs energy of adsorption ΔG°_{ads}, which characterizes the transition of the adsorbate from the standard state in the bulk to the standard state on the surface, was calculated by the formula[7] $\Delta G^\circ = -RT\ln K_1$. Using the known relation $\Delta S^\circ = (\Delta H^\circ - \Delta G^\circ)/T$, we calculated the standard changes in the molar entropy of adsorption ΔS°_{ads}. The relative error of determination of the thermodynamic parameters of adsorption did not exceed 2%.

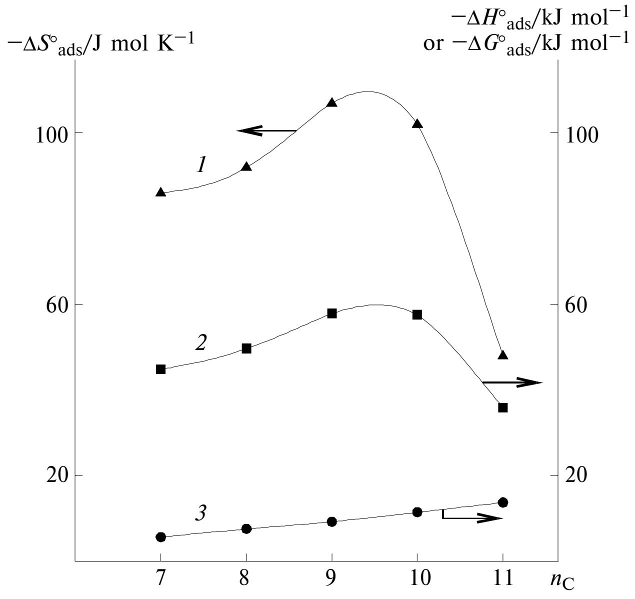


Fig. 3. Thermodynamic parameters of adsorption of *n*-alkanes as functions of the number of carbon atoms (n_C) at 185 °C: $-\Delta S^\circ_{ads}$ (*1*), $-\Delta H^\circ_{ads}$ (*2*), and $-\Delta G^\circ_{ads}$ (*3*).

Table 1. Henry's constants of adsorption (K_1)

Sorbate	K_1/cm^3 g^{-1} at different temperatures (T/°C)				
	135	143	156	172	185
n-Heptane	36.66	31.79	20.09	14.31	8.960
n-Octane	74.65	54.31	36.81	22.79	14.78
n-Nonane	139.9	98.23	60.94	34.91	21.40
n-Decane	230.4	159.2	99.52	57.26	35.31
n-Undecane	—	—	184.6	116.5	73.84
Benzene	32.87	26.68	17.73	12.72	8.951
2-Methylheptane	39.90	32.04	20.12	12.58	10.13
Cyclohexane	32.58	24.91	18.44	11.84	8.490
$CHCl_3$	21.69	17.56	13.05	9.519	6.460
CCl_4	31.58	26.84	19.41	15.91	9.219
$ClCH_2CH_2Cl$	25.47	21.35	15.41	10.86	7.390

Results and Discussion

The obtained Henry's constants are presented in Table 1. As expected, the K_1 values decrease with increasing temperature. The adsorbates can be arranged in the following series in the order of decreasing K_1: *n*-alkanes > *iso*-alkanes > benzene ≈ cyclohexane > chloro derivatives of hydrocarbons. Table 2 contains the thermodynamic parameter of adsorption calculated from the polythermic data. Since the adsorption entropy changes slightly with changing temperature, the ΔS°_{ads} values are presented at only one temperature. The low ΔH°_{ads} values (from −35 to −60 kJ mol^{-1}) indicate physical adsorption with prevailing van der Waals interactions.[8] Table 2 shows that the thermodynamic functions of adsorption for different compounds are close to each other. The exception is *n*-alkanes, for which the Gibbs energy increases with an increase in the length of the hydrocarbon radical, and the increment ΔG°_{ads} is ~2 kJ mol^{-1} per CH_2 group.

The size of the adsorbate molecules has the greatest effect on *n*-alkane adsorption (Fig. 3). As can be seen in Fig. 3, ΔG°_{ads} changes linearly with an increase in the chain length of *n*-alkane. This pattern of increasing Gibbs energy is due to the nonadditive change in the enthalpy and entropy of adsorption with increase in the carbon chain length, and these values demonstrate the compensation effect. Considering the changes ΔH°_{ads} and ΔS°_{ads} for all adsorbates (Fig. 4), we can see that the substances different in nature obey the single correlation described by the equation $\Delta H^\circ_{ads} = 2.906 + 0.567\Delta S^\circ_{ads}$ ($r = 0.998$). The existence of such a correlation agrees with the assumption that the interaction of the adsorbates with the polymer is of the same nature. This correlation (see Fig. 4) is not valid for decane and undecane, whose molecular cross sections, most likely, become comparable with the average size of the polymer pores. ΔS°_{ads} for decane and that for undecane are underestimated by the absolute value. Perhaps, this is because the size of the

Table 2. Thermodynamic functions of adsorption of hydrocarbons and chloroalkanes by polymethylsilsesquioxane

Sorbate	$-\Delta H°_{ads}$ /kJ mol^{-1}	$-\Delta G°_{ads}$/kJ mol^{-1} at different temperatures (T/°C)					$-\Delta S°_{ads}$/J mol^{-1} K^{-1} at 185 °C
		135	143	156	172	185	
n-Heptane	44.8	12.2	11.9	10.7	9.8	8.3	86
n-Octane	49.7	14.6	13.8	12.8	11.6	10.2	92
n-Nonane	57.8	16.8	15.9	14.6	13.1	11.7	107
n-Decane	57.5	19.0	17.9	16.4	15.0	13.6	102
n-Undecane	35.9	—	—	18.6	17.6	16.4	48
Benzene	40.4	11.8	11.0	10.3	9.4	8.3	76
2-Methylheptane	44.1	12.5	11.9	10.7	9.5	8.8	83
Cyclohexane	41.2	11.7	11.1	10.4	9.1	8.2	78
$CHCl_3$	36.6	10.4	9.9	9.2	8.3	7.1	70
CCl_4	36.1	11.7	11.3	10.6	9.9	8.4	66
$ClCH_2CH_2Cl$	38.1	10.9	10.6	9.8	8.8	7.6	73

adsorbent cavity does not allow $C_{10}H_{22}$ and especially $C_{11}H_{24}$ molecules to be incorporated in its cells. As Fig. 3 shows, the $\Delta G°_{ads}$ value for undecane, which falls on the common straight line, can be explained by the compensation of the contribution of the entropy component by the corresponding increase in the enthalpy of adsorption (see Table 2).

Depending on the method of its preparation the structure of PMSS can be either macro-, meso-, or microporous, whereas the micropore sizes are comparable with the sizes of the adsorbed molecules. The adsorption capacity depends on how the sizes of the sorbates match the dimensions of the units forming the free volume of the adsorbent. Evidently, the volume of the cavity of the PMSS under study is accessible for *n*-alkanes C_7—C_{10}, and the size of molecules of higher *n*-alkanes ($>C_{10}$) is comparable with the average pore size, which impedes their adsorption. A similar result was obtained[9] in the study of the adsorption properties of oligosilsesquioxanes. It has been shown[9] that higher alkanes, whose molecular cross section is comparable with the average diameter of the oligosilsesquioxane pores, are predominantly adsorbed on the adsorbent surface. The van der Waals volumes of the pores calculated by the UNIFAK method[10] are <7 Å^3 for all sorbates studied except undecane (7.2 Å^3). Evidently the large size of the undecane molecule prevents adsorption in the micropores, which allows us to classify this adsorbent as microporous.

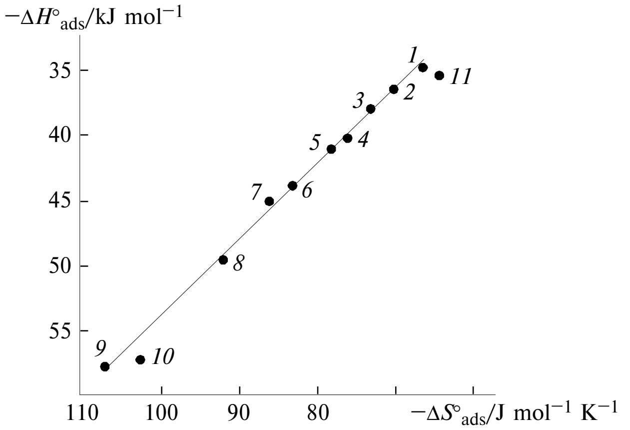


Fig. 4. Correlation of thermodynamic parameters of adsorption for CCl_4 (*1*), $CHCl_3$ (*2*), $ClCH_2CH_2Cl$ (*3*), benzene (*4*), cyclohexane (*5*), 2-methylheptane (*6*), *n*-heptane (*7*), *n*-octane (*8*), *n*-nonane (*9*), *n*-decane (*10*), and *n*-undecane (*11*).

The results obtained suggest that the studied PMSS adsorbent in the region of low coverages is not selective for the compounds studied.

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Received July 28, 1999;
in revised form May 3, 2000