

Chromatographic and molecular statistical studies of structural and energy characteristics of surface micropores of silicates and silica adsorbents

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Abstract - A comprehensive approach to the investigation of structural and adsorption-selective characteristics of surface-porous silicates and silica adsorbents is developed, combining the chromatographic measurements and molecular statistical calculations involving the model pore structure and the detailed molecule-surface interaction potential. The method is capable to describe the non-specific and weak specific adsorption on microporous surface and can be applied to the wide class of microporous adsorbents.

INTRODUCTION

Recent adsorption-structural and chromatographic studies had strongly indicated that surface micropores of disperse substances play much more significant role in the processes of adsorption and chromatographic separation than it was often supposed before. One can consider as an example the data presented in Table 1, where the adsorption-chromatographic characteristics of organo-substituted layer silicates with rigid (kaolinite) and swelling (montmorillonite) structural cells with respect to the hexane and benzene are compared to one another (ref. 1). The increase of the amount of presorbed long-chain modifier in the case of kaolinite leads to usual consequences: both the Henry constant and the heat of adsorption decrease, which can be ascribed to the increase of the degree of the kaolinite surface coverage with the modifying layer.

TABLE 1. Henry constants (K_1) and differential heats of adsorption (\bar{Q}_a), hydrocarbons adsorbed on organosubstituted clays at 130 °C.

Adsorbent	Amount of presorbed modifier (mg-equ/g)	Hexane		Benzene	
		K_1 (μm)	\bar{Q}_a (kJ/mol)	K_1 (μm)	\bar{Q}_a (kJ/mol)
Kaolinite (non-swelling)	0.27	0.09	30.4	0.22	42.3
	0.50	-	-	0.20	38.1
Montmorillonite (swelling)	1.01	0.95	23.4	3.44	31.1
	1.60	1.19	25.5	5.17	30.3

On the contrary, the organo-substituted montmorillonite shows the significant increase of the retention volumes and calculated Henry constant when the modification degree increases, with the heat of adsorption remaining virtually unchanged (Table 1). We had shown (ref. 2) that this behaviour is to be ascribed to the preferential adsorption of the hydrocarbon molecules in long micropores forming on the side surface of the mineral crystallites during the modification of swelling layer silicates.

POROUS SIDE SURFACE OF SWELLING SILICATE: NON-SPECIFIC SORPTION

The results of the structural studies had shown (ref. 3) that in the process of the substitution of metal cations which connect separate layers of the montmorillonite, with the organic alkylammonia cations, the separation between the aluminosilicate layers increases due to the formation of modifier mono- or polylayers in the interlayer gaps. The amount of presorbed modifier for the considered adsorbent is sufficient for each successive block (the aluminosilicate layer covered with modifier monolayer) of such 'multisandwich' structure to be separated from its neighbour by an extra monolayer of organic cations, that is, the interlayer gap is thrice as wide as the alkyl chain width is. Simple structural considerations (ref. 4) show that the intermediate submonolayer is to be more deficient than the monolayers adjacent to the silicate layers, with this monolayer defects concentrating at its boundaries on the microcrystallite surface, thus forming on this surface a system of long parallel micropores. The free cross-section width of the micropores openings is equal to the width of an alkyl chain (0.44 - 0.46 nm), and the length of the micropores is limited by the characteristic microcrystallite size. The silicate layer thickness (0.94 nm) and the width of the alkyl chain tripled amount to the total period (2.2 nm) of such porous structure.

The introduction of uncharged large-size Cs⁺ cations into the exchange complex of the montmorillonite enables one to increase significantly the contribution of the crystallites side faces into the total amount of the mineral external surface (ref. 5), which in turn leads to the enhance of adsorption-separation properties of the resulting adsorbents. We developed the technology of the preparation of selective chromatographic adsorbent based on successive substitution of the montmorillonite exchange complex by the sodium, cesium and cetylpyridinium cations. This adsorbent had shown high selectivity with respect to the chromatographic separation of isomeric alkyl-, alkylchlor-, and chlorsubstituted benzenes (Fig. 1) and in the chromatographic analysis of the multicomponent mixture of the isomers and homologs of hydrocarbons and chlorated hydrocarbons present as the impurities in the technical 1,2-dichlorethane (ref. 6).

To support the considerations about the porous surface structure presented above we had calculated the molecular-statistical estimate of the mean micropore depth using the method developed earlier (ref. 7) for the calculations of the thermodynamic functions of the adsorption of molecules on the periodically inhomogeneous surfaces in the Henry region. The appropriate software was described elsewhere (refs. 7,8). The adsorbent surface was represented as the combination of elemental fragments of atomic sheets and blocks with the number atomic densities and charge densities considered to be homogeneously distributed within, which made it possible to calculate the adsorption potential to within the needed accuracy by the integration of appropriate expressions for atom-atom potentials over the sheet or block fragments and subsequent summation of the different fragments contributions. The symmetry of the model adsorbent surface enabled us to calculate the thermodynamic functions in the course of the integration through two spatial and three angular variables describing the position of the adsorbed molecule with respect to the surface.

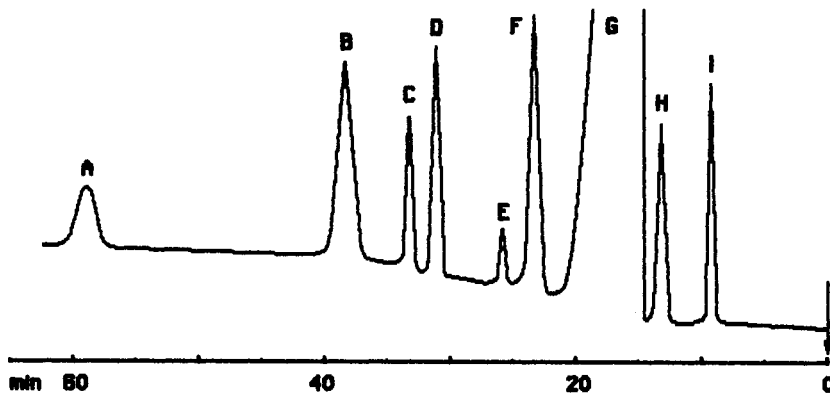


Fig. 1. Chromatogram of technical 1,4-dichlorbenzene (G) and detected organic impurities: 1,2,3-trichlorbenzene (A), tetradecane (B), 1,2,4-trichlorbenzene (C), 1,2-dichlorbenzene (D), 1,3,5-trichlorbenzene (E), 1,3-dichlorbenzene (F), 4-chlortoluene (H) and chlorbenzene (I) on the adsorbent containing 7% Cesium cetylpyridinium montmorillonite, 3% dinonylphthalate; support - Chromatone N-AW-DMCS.

The microscopic adsorbent model was considered in details elsewhere (ref. 4); here we present the brief discussion of the experimental results, theoretical calculations and estimates summarized in Table 2. The software package (refs. 8,9) was used to calculate the thermodynamic characteristics of the adsorption of hexane on the basal (non-porous) modified montmorillonite surface; then from the experimental values, common thermodynamic relations, and structural data (ref. 10) showing that total basal surface is equal approximately to the total side surface, it was straightforward to estimate the thermodynamic functions values characteristic to the side (microporous) adsorbent surface.

TABLE 2. Experimental, calculated and estimated values of Henry constant K_1 and differential heat of adsorption \bar{Q}_a for hexane adsorbed on montmorillonite modified by cetylpyridinium (0.75 mol/kg) at 120 °C.

Parameters evaluation method and conditions	K_1 (μm)	\bar{Q}_a (kJ/mol)
Experiment	0.60	36.4
Calculation for basal (non-porous) surface	0.12	29.7
Estimate for side surface	1.1	37.2
Calculation for side surface:		
Pore depth = 0 nm	0.132	30.0
Pore depth = 0.4 nm	0.027	29.5
Pore depth = 0.55 nm	0.275	41.1
Pore depth = 0.7 nm	5.053	75.1

Next we performed the series of the calculations of the thermodynamic functions of adsorption on model microporous surface with different values of mean pore depth. Comparing the calculated values with the estimated ones it can be seen that the $K_1 \sim 1.1 \mu\text{m}$ value corresponds to the mean pore depth of the order of 0.6 nm, while the \bar{Q}_a matching requires a slightly less depth value of 0.5 nm. An \bar{Q}_a independent estimation (ref. 4) of the mean pore depth based on the comparison of the specific surface values with respect to the hexane for the non-modified and alkylpyridinium-modified montmorillonite (ref. 11) leads to the pore depth value of the order of 1 nm being in good correspondence with the molecular-statistical estimate above.

Thus the molecular-statistical calculation based on the specified microscopic model of the side surface of swelling layered silicate with one adjustable parameter only - the mean pore depth, leads to a quite satisfactory agreement with the experimental data, supporting the reliability of the model assumptions concerning the surface structure of modified layer silicates.

ADSORPTION IN LONG MICROPORES: POLARIZATION INTERACTION

Much more wide is however the class of the adsorbents for which the adsorbed molecules interact directly with the inorganic mineral surface. In this case the account for the dispersion attraction and short-range atom-atom repulsion would not suffice, and the polarization interaction is expected to play a major role. The corresponding approach will be demonstrated using the molecular-statistical interpretation of the experimental data (ref. 5) for the thermodynamic characteristics of adsorption of *n*-hexane on the microporous surface of the palygorskite dehydrated at 120 °C.

The structure of the ribbon-layered silicate, the palygorskite, is built of staggered blocks. The block is formed by two networks of silicone-oxygen tetrahedra, connected by the octahedral network containing hydroxyle groups and coordinately linked water molecules (ref. 12). Thus the chessboard-like cross-section of the crystal contains the blocks and channels, with the channel crystallographic dimensions for the palygorskite dehydrated at 120 °C being equal to 0.90 × 0.65 nm, corresponding to the free section of 0.64 × 0.37 nm. These channels are too small for the linear hydrocarbon molecules to penetrate into, and the adsorption takes place preferentially on the external mineral particle surface (ref. 13).

This external surface can be considered as formed by the destruction of the crystal along the edges of the ribbons, i.e. the breaking of the weak edge Si-O-Si bonds with subsequent saturation of the released valence bonds by the protons. The resulting surface possesses the repeating microporous relief, with the surface micropores characterized by the width of 0.70 nm (the crystallographic channel width without doubled OH-bond length) and the depth of 0.65 nm. The adsorbate molecules contact directly with the silicate surface, and for the system considered the polarization contribution into the total potential energy value cannot be neglected, this contribution being created by the electrostatic field of the adsorbent surface resulting from the distribution of charges, in particular, from the polar SiOH groups located on the micropore edges, and from the water molecules linked with coordinately unsaturated Mg⁺ cations - at the pore walls.

It makes no special difficulties to incorporate the polarization interaction into the calculation scheme described above as the corresponding contribution into the adsorption potential which depends on the electrostatic field created by the surface atomic charges, and on the polarizabilities of the adsorbate atomic species can be calculated by summation over the contributions of the lattice fragments.

To determine the charges of lattice ions the quantum-chemical MNDO calculations were performed. Two cells were considered, with and without an isomorphic substitution Al → Si in the basal tetrahedral layer, the compensating Na⁺ ion being introduced in the substituted cell. The average values of charges used for the molecular-statistical calculations were obtained assuming that the relative percentage of both types of cells in the lattice is 1:7 (ref. 14). The average charges were -0.61 *e* for the oxygen ions in the tetrahedra, +1.40 *e* for the Si⁺ and Al⁺ ions in the tetrahedral coordination, +0.25 *e* for the H ions compensating the broken bonds on the edges, and -0.25 *e* for the intralayer hydroxile groups. The compensating Na⁺ ion charge was

found to be +0.50 e, thus the average compensating ion charge per unit cell was taken equal to +0.06 e. The atomic charges of the bonded water molecule were set equal to those of the free water molecule, the average charge for the ions in the octahedral coordination was found from the electroneutrality requirement.

Table 3 summarizes both the experimental data (ref. 5) and our theoretical estimates of the adsorption heat. It is seen that the polarization interaction contributes significantly to the total value, cardinaly improving the agreement between the observed and calculated characteristic. The two values shown in the table for the polarization interaction differ in that the more accurate one was obtained in the approximation where the charge distribution in the immediate vicinity of the pore was accounted for using the homogeneously charged atomic lines, while that giving a slightly worse value involved the homogeneously charged atomic sheets approximation. Thus as the thermodynamic characteristics obtained depend significantly on the presence of the polarization interaction component, being insensitive enough to the detailed profile of the adsorption potential, one may conclude that a good agreement observed between the calculated and measured values is not accidental and presents a strong evidence supporting the correctness of the model used.

TABLE 3. Differential heat of adsorption (kJ/mol) of *n*-hexane on palygorskite surface at 400 K.

Polarization interaction excluded		48.0
Polarization interaction included:	atomic sheets	88.3
	atomic lines and sheets	83.6
Experiment		78

Here again the molecular-statistical method based on the microscopic model of the microporous adsorbent leads to a rather satisfactory agreement with the experiment provided the essential interactions of adsorbed molecule with the adsorbent surface, including the polarization and dispersion attraction and short-range atom-atom repulsion, were taken into account.

ORGANOSILICONE MODIFIER OF DISPERSE SILICA: PORE SELECTIVITY

We developed also the methods of the preparation of high-quality chromatographic supports based on disperse silica and organosilicone modifiers. The fact that these supports proved to be efficient for the separation of the mixtures of C_{10} - C_{18} alcohols (Fig. 2) and the data presented in Table 4 showing the sharp decrease of the specific heats of wetting q and an increase of the water molecular area ω_{H_2O} for the modified support as compared to the initial one, indicate that the surface of prepared supports is highly deactivated.

TABLE 4. Physico-chemical characteristics of initial and polymethylhydridesilicone-modified silica.

Silica modification method ^a	S_{Ar} (m ² /g)	a_m (mmol/g)			ω_{H_2O} (nm ²)	q (mJ/m ²)	Thermo-stability in N ₂ media (°C)
		C_8H_{18}	C_8H_{16}	H_2O			
I	44.0	0.133	0.185	0.350	0.208	250	-
V	31.0	0.101	0.104	0.017	3.04	36	300
T	120.0	0.126	0.140	0.022	9.90	22	600

^a I = initial, V = vacuumation, T = thermooxidation.

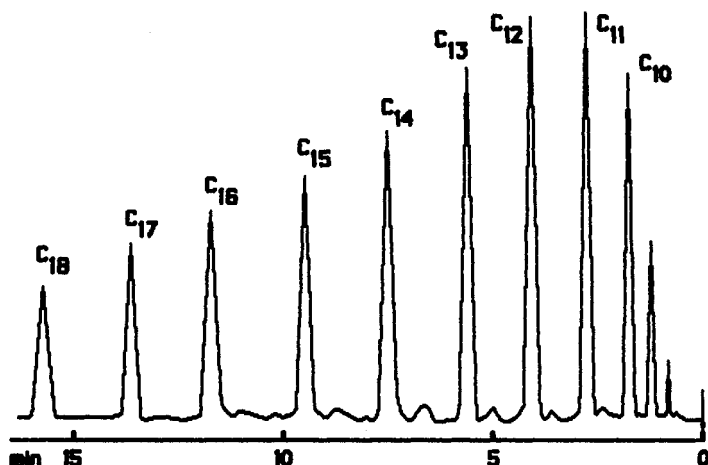


Fig. 2. Chromatogram of mixture of alcohols on the column containing 5% silicone rubber and diatomite support modified by polyethylhydridesilicone.

An important performance characteristic of the supports, the thermal stability, was further improved using the thermooxidation of the modifying layer at 300 - 350 °C. The splitting out of the organic radicals made it possible to increase significantly the degree of 'sewing together' the chemisorbed oligomer molecules, leading to the decrease of the adsorption activity of the modified support, as the residual hydrophilic centers on its surface became virtually blocked off (Table 4 data show the decrease of the q and the increase of the W values for the thermooxidated sample as compared to the one modified without the thermooxidation). The thermooxidation of the modified layer provides also the sharp increase of the thermal stability of the product due to the bonding of the silicone atom with three oxygen atoms. However it is seen from Table 4 that both the specific surface of the thermooxidated sample with respect to the argon and its adsorption capacity with respect to the benzene increase significantly, indicating that surface micropores are formed in the modifying layer.

To determine the size of surface micropores we used the gas chromatographic version of the molecular probing method, based on the comparative analysis of the thermodynamic characteristics of adsorption for the molecules with known size incapable to interact specifically with the atoms located on the adsorbent surface. The experimental results are summarized in Table 5; it is seen that the retention volume of the *iso*-octane decreases significantly with respect to that of the *n*-heptane while the \bar{Q}_a values are close to each other. At the same time for the adsorption ^a on the organosubstituted layer silicates and on the macroporous silicates these characteristics remain virtually the same. It enabled us to conclude that the effective diameter of surface micropores in the thermooxidated sorbent matches the equilibrium cross-section of the *iso*-octane molecule (0.70 - 0.75 nm).

To study the selective properties of the microporous adsorbent with respect to the hydrocarbons the software package was developed implementing a version of the molecular mechanics method, the optimization of the total energy represented as the sum of pure electrostatic interaction, the dispersion and polarization attraction, and short-range atom-atom repulsion with respect to the position and orientation of the molecule near the adsorbing surface fragment. In the optimization run the profile of the potential well was determined,

thus enabling one to calculate the thermodynamic functions of adsorption in the Henry region. Using this package the thermodynamic characteristics of adsorption of linear alkanes and *iso*-alkanes on model quasihomogeneous silicate surface and in model surface micropore were calculated.

TABLE 5. Adsorption of hydrocarbons and CCl_4 on surface-porous diatomite adsorbent at 130 °C.

Adsorbate	Molecule cross-section (nm)	Retention volume (cm^3/g)	Heat of adsorption (kJ/mol)	Heat of adsorption increment (kJ/mol)
<i>n</i> -pentane	0.43 - 0.49	3.2	39.6	} 6.4 } 9.6 } 3.1
<i>n</i> -hexane	- " -	6.8	46.0	
<i>n</i> -heptane	- " -	15.7	55.6	
<i>n</i> -octane	- " -	32.5	58.7	
<i>iso</i> -hexane (2-methylpentane)	0.56	4.8	45.7	
<i>iso</i> -octane (2,2,4-trimethylpentane)	0.70	7.7	54.4	
CCl_4	0.60 - 0.65	6.9	46.0	

For the model surface micropore the faujazite crystal structure element was adopted, the incomplete type I 14hedron, or the topped octahedron (ref. 15). This pore possessing the crystallographic cross-section of about 0.85 nm was supposed to model the surface structure formed in the process of the thermooxidation of the silica surface modified by polymethylhydridesilicone. The quasihomogeneous surface was modelled by the structure formed by doubled 6-membered oxygen rings packed onto the plane surface. The values of the microscopic parameters necessary for the polarization energy calculations (the molecules and surface fragments ionization potentials and atomic charges) were obtained from the MNDO quantum-chemical calculations.

TABLE 6. Adsorption of hydrocarbons at 400 K on model quasihomogeneous silica surface and in model surface micropore: k the dimensionless Henry constant, \bar{Q}_a (kJ/mol) the differential heat of adsorption.

Adsorbate	Quasihomogeneous surface		Surface micropore	
	$\ln(k)$	\bar{Q}_a	$\ln(k)$	\bar{Q}_a
<i>n</i> -butane	-2.11	28.7	-0.90	57.1
<i>iso</i> -butane	-2.17	27.2	-1.01	53.4
<i>n</i> -pentane	-0.38	48.0	1.92	63.6
<i>iso</i> -pentane	-0.50	45.6	0.51	66.2
<i>neo</i> -pentane	-0.93	41.3	2.19	68.7
<i>n</i> -hexane	1.12	57.9	1.36	63.7
(2,3)-dimethylbutane	0.82	55.2	2.71	66.9
cyclohexane	-0.51	44.9	3.93	69.0

The results summarized in Table 6 show that the method developed is capable to describe the selective properties of surface micropores with respect to the hydrocarbons adsorption. It is seen that on model homogeneous surface the adsorption obeys usual rules: the increase of the alkyl chain length leads to the monotonous increase of the Henry constants and the heats of adsorption. In the model micropore the

adsorption is in fact determined by the correspondence between the Van-der-Waalsian sizes of the molecule and the micropore: for the optimal matching of the pore by the pentane molecule the peak of the adsorption characteristics is reached, and with further increase of the alkyl chain length these characteristics decrease. The cyclohexane molecule also matches our model micropore extremely fine, which results in high calculated values of the adsorption characteristics.

The results of the calculations are in qualitative agreement with the experimental data for the thermodynamic characteristics of normal and *iso*-alkanes adsorption on surface-porous adsorbents synthesized on the basis of silicas and perlites. This leads one to the conclusion that the molecular-statistical model approach to the description of the adsorbents surface structure and adsorption properties is non-contradictory and can be developed further to study the behaviour of these systems in more details. In particular, the preliminary calculations we made for more realistic surface micropores structures including other zeolite framework elements, e.g. distorted incomplete 26hedra and 18hedra (ref.15) indicate that it is possible to reproduce more accurately the selectivity characteristics of the hydrocarbons adsorption on such surfaces.

CONCLUSIONS

The results presented here strengthen the view that the combination of the chromatographic and molecular statistical methods provides a powerful tool for the investigation of structural and adsorption-selective characteristics of surface-porous silicates and silica adsorbents.

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