

Chromatographic methods in solid surface investigations

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Abstract - The application of chromatography as a testing method for properties of surfaces is considered. Examples are provided of employing chromatography for studying the geometry and surface chemistry of solids and sorbents of various nature, such as non-porous silica, non-porous ionic adsorbent on barium sulfate base, porous γ -iron oxide and polymer sorbents. The high sensitivity of the chromatographic method in investigating the changes in the texture and the chemical state of the surface are shown.

INTRODUCTION

Chromatography, due to its inherent ability to intensify manifestation of intermolecular interactions as a result of multiple reiteration of the adsorption-desorption acts in the chromatographic systems, opens up great potentials for developing methods of testing the properties of surfaces. An application involving molecules of practically any type as test-substances makes it possible to investigate finest mechanisms of interaction inaccessible with any other method. For instance, in gas chromatography, at separation coefficient equal to 1.14 and efficiency chromatographic system 1000, theoretical plates differences in thermal effects in approximately 300 J/mol can be measured. Taking account of the fact that the efficiency of chromatographic columns can be comprised of thousands of theoretical plates (e.g. in capillary columns), one can imagine how small differences in intermolecular interactions can be measured.

The advantages of chromatography are as follows: high sensitivity, the possibility of investigation within a wide range of temperatures, speed of measurements made with standard equipment, and the simplicity of automating the research. An application of capillary columns for physico-chemical research (ref. 1) increases the precision of retention parameters measurements significantly, enables work with micro-gram quantities of a substance, including chemically unstable substances. In this case ideal conditions exist for measuring the diffusion coefficients of gases, liquids and polymers. The disadvantages of chromatography in physico-chemical measurements are mostly due to the problems of mass-transfer of adsorbates and reaching the equilibrium. For investigating the surface properties of solids, especially those featuring small specific surfaces, the method of gas chromatography is the most sensitive. Introduction of highly sensitive detecting systems into chromatographic practice makes it possible to work with highly diluted samples when the concentration of the adsorbate molecules in the gas phase and on the surface is extremely small. This makes it possible to neglect an interaction of the adsorbed molecules between themselves and confine the study to their interaction with the surface of the solid. Gas chromatography makes it possible to determine specific retention volumes $V_{g,1}$ for symmetrical peaks and retention volume calculated per adsorbent unit area $V_{a,1}$ for small (practically negligible) amounts of adsorbates. In equilibrium chromatography and in practically non-adsorbed gas, $V_{a,1}$ is the Henry constant K_1 of the adsorption equilibrium, i.e. the initial slope of the adsorption isotherm on the surface of a solid (ref. 2,3). Besides the Henry constant, the differential change of the adsorption internal energy can also be measured from the relation in $V_{a,1}$ of $1/T$ which is equal to the heat of adsorption, a differential change of the free energy and a differential molar change of the entropy of adsorption. Gas

chromatographic study of large coverages of the surface makes it possible to determine the adsorption isotherms at different temperatures and calculate the dependence of adsorption heat on the coverages of the surface from isosters (ref. 4-6). Liquid chromatography also makes it possible to investigate interaction accompanying adsorption from solutions on solid surfaces of various nature; to determine K_1 and adsorption isotherms (ref. 7,8).

In addition to general thermodynamic characteristics of the adsorbate-adsorbent interaction, chromatography enables to investigate very fine effects of interaction. For instance, chromatographic methods are applied to describe the texture of the surface, determining the amount and the nature of the active centers on the surface, their changes in the course of treatment of the materials, as well as the beginning of catalytic transformations, etc. (ref. 9, 10). In the investigation of the changes of the surface texture, retention of substance is measured, whose adsorption is sensitive to geometry of the surface, presence of protrusions, edges featuring increased adsorption potential on the surface. Usually, alkanes and naphthenes are used as such substances. When the chemical state of the surface is studied, retention of polar substances is usually determined which are sensitive to the presence of active centers of various nature on the surface as well as to the type of intermolecular interactions.

The choice of test-substances is of utmost importance, these are organic molecules with certain functional groups. Usually the following substances are used for the purpose:

1. n-Alkanes and naphthenes capable only of non-specific interaction and testing this interaction. The type of interaction of the molecules of these substances features a possibility of the surface to provide conditions ensuring this type of interaction. That is why they are convenient for testing the surface texture and the control of its changes as a result of an impact over a solid body.
2. Aromatic substances, benzene in particular, test π -complex formations;
3. Alcohols interact with electron-donor groups of the surface with a hydrogen bond evolving;
4. Ketones containing donor groups test donor-acceptor complex formation;
5. Nitro-containing substances act as electron acceptors, testing the orientation interaction ($\mu = 3,6$ D) and development of donor-acceptor complexes;
6. Amines (e.g. pyridine) develops a hydrogen connection with H-donors also testing the donor-acceptor complexes.

An application of this set of test-substances as adsorbates leads to conclusions on the physico-chemical state of the surface of a solid.

This paper shows an acceptability of the methods of chromatography for testing properties of the surface through its application to the investigation of surfaces of various nature:

1. Non-porous silica (specific surface area $S < 1$ m²/g)
2. Non-porous ionic adsorbent on the basis of barium sulfate (S from 2 to 10 m²/g)
3. Porous γ -Fe₂O₃ ($S = 21$ m²/g)
4. Porous polymer sorbents containing various functional groups (S from 20 to 200 m²/g).

1. NON-POROUS SILICA

Gas chromatography is applied to investigation of the surface state of silica in the process of its modification. Fig. 1 provides values for $V_{g,1}$ of the test-substances on the original silica ($S < 1$ m²/g) and silica modified by Trilone B (disodium salt of ethylene diaminetetraacetic acid). As seen from the figure, the surface of the silica is covered by a certain number of OH-groups (alcohol, ketone, pyridine) which are noticeably retained due to formation of hydrogen bonds. Rather

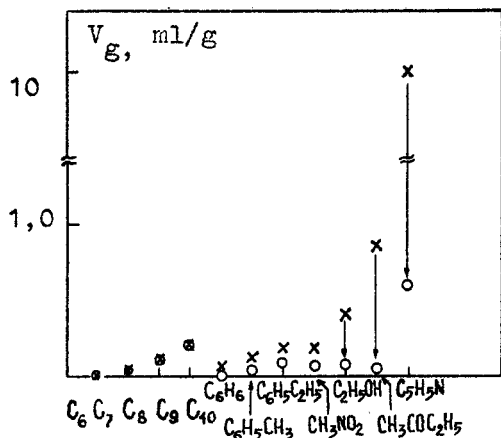


Fig. 1 Values for $V_{g,1}$ of the investigated substances on silica (x) and its modification (o) at 80°C. The abscissa provides the names of the substances under investigation. The column is 110 cm in length, with a diameter of 3 mm.

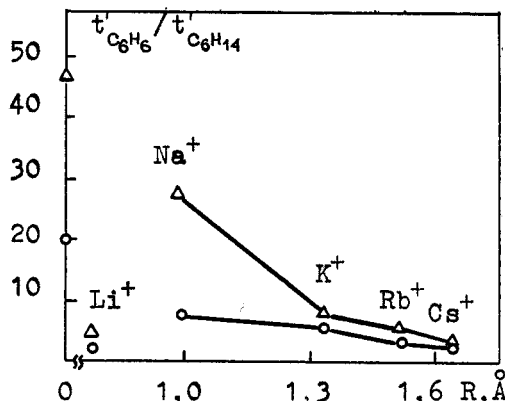


Fig. 2. An effect of the radius of the modifying cation on the specificity of BaSO_4 samples (2.3 m^2/g (o) and BaSO_4 - 8 m^2/g (Δ) at 140°C, t' is an adjusted retention time.

symmetrical peaks testify to the energetic homogeneity of the surface. Among the polar substances, the maximal adsorption energy is revealed for methyl-ethylketone (69 kJ/mol). Modified by Trilone B, silica does not change the $V_{g,1}$ of n-alkanes, i.e. S of the sample and the dispersion interaction between the adsorbate and the solid do not change with silica modification. Very insignificantly retained by the modified surface are polar molecules including fragments of non-divided electronic pairs or π -bonds and molecules having their electronic density concentrated in one of their centers in their functional groups with a decrease of the density at the other one (according to A.V. Kiselev's classification, they are B and D-group molecules) (ref.2). For instance retention of nitromethane decreased 5 times, of ethyl alcohol 13 times, of methylethylketone 40 times compared to the initial silica (with the accompanying decrease of the adsorption energy by 16, 14 and 20 kJ/mol, respectively); retention of pyridine decreased 16 times with the adsorption energy showing an increase by 9.3 kJ/mol. So, in modifying silica by Trilone B screening of active centers of adsorption for specific adsorbing molecules occurs, (various types of OH-groups, coordination-unsaturated silicon atoms) (ref. 11), the modified surface develops new active adsorption centers featuring a stronger energy of adsorption bond with organic bases.

2. NON-POROUS IONIC ADSORBENT ON THE BASIS OF BARIUM SULFATE

Barium sulfate is an ionic adsorbent (the adsorbent according to A.V. Kiselev's classification of the II type) (ref. 2, 12). Barium cations on its surface are the sites of concentration of the positive charges which are centers of prevailing adsorption of electron-donor substances. The negative charge is distributed around SO_4^{2-} large complex anions and so the contribution of anions into the adsorption of polar molecules is minimal. Gas chromatography methods were used to investigate the change in the condition of BaSO_4 surface in the process of modification with inorganic salts, which is important for its application in analytical practice (ref. 13). Modification was done with chlorides of alkaline metals. Fig. 2 shows an effect of the radius of the modifying cation on the specificity of BaSO_4 samples.

Gas chromatography method was applied for the purpose of estimation of the optimal amount of NaCl from the solution on the BaSO_4 surface. Earlier attempts to apply various physico-chemical methods (e.g. the ESCA method) failed. The Kováts indices RI (ref. 14) for benzene at 150°C on pure BaSO_4 -8 m^2/g is equal to 950 u.i. and falls to 893 u.i. when the concentration of the modifying salt in the solution equals 20%. The RI gauging dependence on the amount of the modifying salt is equivalent to 0.1-0.2% of the weight of NaCl on the surface. Most complete elimination of energy and geometric non-homogeneity of BaSO_4 occurs which can be detected and estimated from the shape of the chromatographic peaks and the values of the thermodynamic characteristics of adsorption for substances of various nature (ref. 15).

3. POROUS γ -IRON OXIDE

Separate effects of the structure and surface chemistry on the adsorption of a substance was observed in the investigation of γ -iron oxide subjected to a dialysis treatment for the purpose of purifying from contaminating additives. The powder was used for 5 series of measuring the temperature dependence of benzene and hexane retention within the temperature range between 50 and 200°C. Fig. 3 presents the ratios of $\lg(V_{g,1}) = f(1/T)$ for hexane and benzene obtained in the five series of measurements. Non-polar sorbates feature a non-linear dependence for the whole of the temperature range with a gradual decrease of $V_{g,1}$ at the stage of transition from one series of measurements to another, with $V_{g,1}$ stabilizing at all temperatures reached in the 4-5th series of measurements. The slope angle for the lines increases gradually in the 1st-3rd series of measurements, hence, reveal the increase of the adsorption heat for alkanes being constant for series 4 and 5. On the basis of the data, for the alkane adsorption one may consider that the surface structure of purified γ -Fe₂O₃ stabilizes gradually and does not change at later stages of work. Unlike n-alkanes testing the changes of the surface structure of the adsorbent exclusively, the adsorption of electron-donor molecules of benzene, sensitive also to changes of the surface chemistry is characterized by a number of additional specific features. Firstly, there is a transition from the physical to activated adsorption of benzene molecules determining the minimal curves observed at the ratios at the temperatures of 150-160°C. Secondly, in the three initial series there is a downward shift of the temperature curves for benzene observed simultaneously with n-alkanes. However, unlike the n-alkanes, which develop stabilized adsorption characteristics, with $V_{g,1}$ at the transition stage from the 3rd to the 5th series. It becomes vivid in the $V_{g,1}$ graph depending on the number of the sequence (Fig. 4). Starting at a certain moment, non-specific interactions with γ -Fe₂O₃ surface terminate showing any dependence on the length of the heating period which specific interactions continue to change. On the basis of these data supported by the mass-spectrometry data obtained in the analysis of the gas-release products, a conclusion was made assuming that γ -iron oxide after the dialysis purification had an amorphous deficient structure.

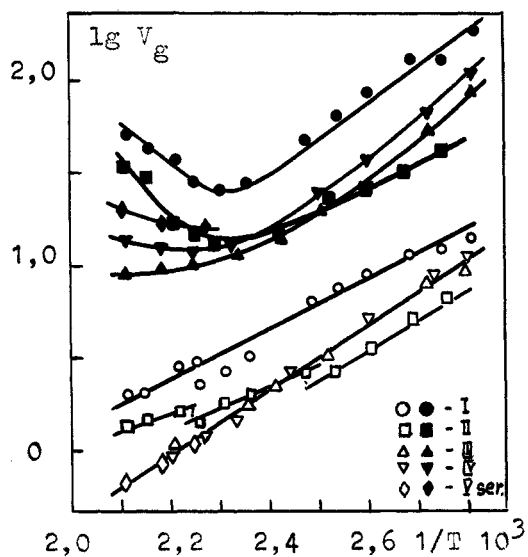


Fig. 3 Dependence of $\lg V_{g,1}$ of hexane (open circles) and benzene (filled circles) on $1/T$ in five series measurements on dialysis-treated γ -iron oxide

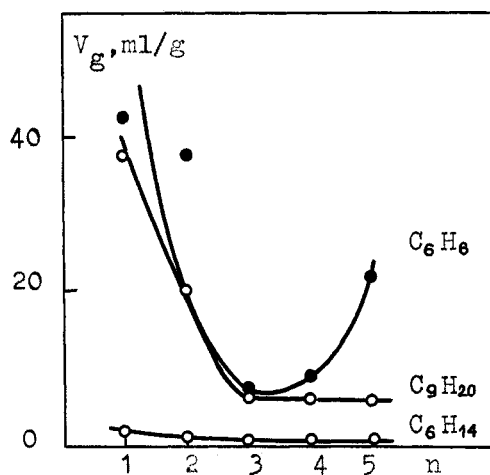


Fig. 4 Dependence of $\lg V_{g,1}$ of hexane, nonane and benzene on the number of measurement series on dialysis-treated γ -iron oxide at 200°C.

Heating of the adsorbent at the temperature of 200°C resulted in its additional purification from volatile impurities and molecular-adsorbed water with a simultaneous reconstruction and stabilization of the structure surfaces. Testing surfaces of solids by adsorbates of various chemical nature, as was mentioned earlier, is often implemented not only for the purpose of a qualitative description of the surfaces, but also for quantitative calculations of, for instance, the number of active adsorption centers. It is especially convenient for energy-level highly active surfaces, of which γ -iron oxide is a good example. Applying the method of contaminating the surface by irreversibly sorbent substances of the acidic or base nature, and then, depending on the applied "poison" and its amount, the nature

and the number of centers are determined. In gas chromatography, *n*-butylamine, acetic acid, propylene oxide, propyl alcohol were used as polar poisons (ref. 16), acetonitrile (ref. 17) diethyl ether (ref. 18), triethanolamine (ref. 18).

In our work, we applied liquid chromatography for investigating stearic acid, as well as phenol and aniline (ref. 19).

Very first doses of the substances introduced into the column were irreversibly sorbed on the surface of the γ -iron oxide. Only upon saturation of the respective adsorption centers on the surface, the peak of the sorptive starts being registered by the detector. Phenol and stearic acid are sorbed at the base centers, while aniline and octadecylamine are sorbed on the acidic centers. Since the total amount of the irreversibly sorbent substance is known as the difference between the introduced and eluated amount, the number of active centers was calculated (Table 1).

4. POROUS POLYMER SORBENTS CONTAINING VARIOUS FUNCTIONAL GROUPS

Reverse gas chromatography method is successfully applied for investigating the interaction in the gas - porous polymer system. The availability of epoxy- and epithio - groups in copolymers 2,3-epoxypropylmethacrylate with ethylenedimethacrylate (GO) and epithiopropylmethacrylate with ethylenedimethacrylate (GS) makes it possible to obtain a wide range of sorbents on their basis of various geometric structure featuring various functional groups (butyl - C4, dodecyl - C12, hexadecyl - C16, nitrile - CN, polyethylene glycol - PEG and amino-groups - EDA and DEA (ref. 20, 21). Gas chromatographic study of these sorbents made it possible to establish a dependence of sorption properties of polymers on the size of their specific surface area and the number of functional groups as well as the nature of the modifying functional groups.

In order to ensure a more detailed analysis of the sorption properties of the surface, a regression equation was suggested which connects the molecular physico-chemical characteristics of sorbates and their geometric structure with gas chromatographic properties of retention (the Kováts indices RI, in particular) (ref. 22, 23).

$$RI = K_1 D_0 + K_2 D_0 \left(- \frac{2}{3 kT} \mu^2 + \alpha G \right) + K_3 D_0 W_a + K_4 D_0 W_d + K_5 \quad (1)$$

where α is a polarizability of a sorbate molecule, μ is its dipole moment, W_a and W_d are electron-acceptor and electron-donor properties, respectively, G is a steric factor taking account of the molecule branch-off and D_0 is a coefficient taking account of the energy non-homogeneity of the index unit on different sorbents.

Fig. 5 provides a correlation between the experimental and the calculated indices Kováts RI obtained from the equation (1) for GS-EDA sorbent (data for 23 substances were processed, the obtained correlation coefficient was equal to 0.985). The regression analysis of the experimental RI for a representative group of sorbates of various chemical nature, whose molecular properties are known, allows us to calculate the $K_1 - K_4$ coefficients which are to be proportional to the mean data for the

Table 1. The number of active centers on the surface of γ -Fe₂O₃

Substance	Type of centres	Number of AC/m ²
Phenol	base	1.1×10^{17}
Aniline	acidic	3.5×10^{17}
Stearic acid	base	1.3×10^{17}
Octadecylamine	acidic	2.2×10^{17}

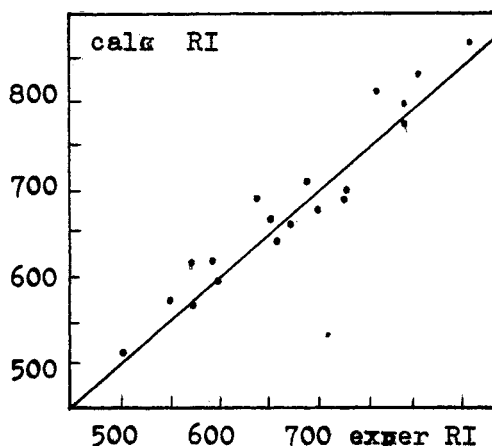


Fig. 5 Calculated vs. experimental RI values on GS-EDA sorbent at 150°C.

Table 2. Coefficients and correlation of the calculated and experimental Kovats RI for the Sorbate testing group.

Sorbent	K_1	K_2	K_3	K_4	K_5	r
Porapack Q	130	16	14	-1	154	.995
Porapack QS	158	19	14	0	120	.999
Porapack S	182	29	33	-1	111	.997
Porapack P	138	29	16	16	89	.999
Porapack R	175	30	38	-1	120	.999
Porapack N	180	40	35	3	127	.999
Porapack T	156	52	42	11	102	.999
GTCB	108	0	0	0	67	.991
Chromosorb 102	144	17	11	1	146	.999
Chromosorb 101	125	26	14	13	104	.999
Chromosorb 105	177	27	27	3	98	.999
Chromosorb 104	132	69	43	21	94	.999
BaSO ₄	83	147	203	102	443	.960
GO	125	42	39	29	136	.997
GO-CN	121	41	43	57	172	.999
GO-DETA	114	45	54	65	197	.998
GO-PEG	118	67	77	16	127	.991
GS	143	30	38	38	133	.991
GS-EDA	132	59	68	58	150	.996
GS-EDA-Cu ²⁺	134	33	41	84	132	.999
GS-EDA-Ni ²⁺	145	36	53	92	138	.999

whole of the surface average molecular properties of the adsorption centres: polarizability - K_1 , dipole moment - K_2 , electron-donor - K_3 , and electron-acceptor capacity - K_4 . Thus, by the way of using the values of these coefficients, changes in the sorbents with respect to manifest various types of intermolecular interaction can be described. The data obtained for various methacrylate polymer sorbents, GTCB and BaSO₄ are provided in Table 2. For non-polar GTCB all "specific" coefficients are equal to zero. Increased values of the K_2 and K_3 coefficients are typical of Porapacks as the original styrene-divinylbenzene matrix is modified by electron-donor agents featuring a noticeable dipole moment (vinylpyridine, vinylpyrrolidone, ethylenedimethacrylate). The acceptor properties practically do not enhance. The differences in the coefficients obtained for Chromosorbs 101, 102 and 105 are evidently accounted for by the different amounts of the styrene groups in the copolymer compositions. It is connected to the fact that the mean physico-chemical characteristics of a sorbent (hence, also the Kovats RI) change as the composition of a copolymer changes. In the series of Chromosorbs 100, Chromosorb 104 is the most polar one. Its value for K_3 and especially for K_2 are high due to the presence of the electron-donor CN-group with a high dipole moment ($\mu = 3.94D$). Some electron-acceptor capacity of the sorbent can be accounted for by the presence of a partly positive charge on the atom of Carbon in the CN-group. For methacrylate sorbents the highest values for K_2 and K_3 emphasising the property of the sorbent to orientation and electron-donor interactions are ensured by the ether-groups in the GO-PEG polymer.

A high donor capacity of amine-containing polymers (GO-DETA and GS-EDA) are accounted for by the presence of a couple of undivided electrons within the N atom in the amine-group. Polymers having nitrile (GO-CN) and amino-groups (GO-DETA and GS-EDA) manifest a high acceptor capacity (K_4) which can be accounted for by the presence of a partial positive charge on the C-atom in the CN-group and on the hydrogen atoms in amino-groups.

The presence of metal cations in the GS-EDA sorbent results in a sharp increase of electron-acceptor properties of a sorbent, which is manifested in the increase of the K_4 coefficient. Simultaneously a decrease of the K_2 and K_3 values observes which can be accounted for by developing cations of transition metal complexes with electron-donor amino-groups of the sorbent which causes changes in the donor-acceptor properties of the surface.

The K_1 - K_5 available coefficients make it also possible to estimate the contribution of every type of the sorbate-sorbent interactions into the general retention since this contribution is determined by

multiplication of the respective sorbent coefficient and the molecular-parameters of the sorbate. Contributions of every type of the sorbate-sorbent interactions into the Kováts RI of the Rohrschneider test substances were calculated on the non-polar Porapak QS, polar Chromosorb 104 and strongly polar GS-EDA sorbent (ref. 22,23).

Investigation of these contributions shows that they are quite comparable in their values. Thus, the Kováts RI disintegration into its components describing various types of interactions makes it possible to have a more detailed and precise determination of how the surface chemistry of the sorbent changed compared to the use of the simple difference between the sorbate retention on the polar and non-polar sorbents.

The examples provided show wide opportunities for applying chromatography in the investigation of surfaces.

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