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Effect of Fluorination on the Surface Properties of Carbon Materials as Probed by Gas Chromatography

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Abstract—The surface properties of graphite, carbon fiber, and their fluorination products were studied using gas chromatography. The retention volumes and Kovatz indices for saturated and aromatic hydrocarbons and oxygenated and nitrogenated compounds were determined. Regardless of the properties of the matrix, fluorination produces materials with chemically homogeneous and apolar surfaces. For fluorinated graphite, the decrease in the retention of branched alcohols compared to that of linear alcohols is more significant than for fluorinated carbon fiber.

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The progressive improvement of techniques for the synthesis of fluorinated carbon derivatives (fluorocarbons) and the substantiation of their scientific and engineering applications is a rapidly advancing field of carbon chemistry. Along with familiar applications of fluorocarbons in the manufacture of high-efficiency antifriction materials and cathodes for energy-intensive chemical current sources [1–3], there are indications [4–8] of the feasibility of their successful application in sorption, catalysis, and chromatography; in particular, fluorocarbons can be successfully used in these fields on account of their extremely high hydrophobicity, thermal stability, and chemical and biological inertness. However, there are several factors, in particular, the nonexistence of detailed data on the adsorption characteristics of such materials, that hinder the design of fluorocarbon-based supports, coatings, and sorbents; the improvement of their manufacturing technology; and the prediction of their surface properties. Gas chromatography is known as one of the most informative investigation tools for surface chemistry and adsorption interactions. With rare exceptions [7–9], however, the potential of gas chromatography with regard to fluorocarbons remains practically unused.

In this work, we use gas chromatography in the Henry region, i.e., at ultimately low surface coverages, to study the surface properties of graphite (G), carbon fiber, and the products of their fluorination using organic compounds of various classes as probe molecules.

EXPERIMENTAL

Characteristics and notations for the test samples are listed in Table 1. We used active graphite (GT grade, State Standard (GOST) 4596-75, particle size of 200–300 μm). Graphite was treated with aqua regia in order to free it from mineral impurities, then washed with distilled water to neutral reaction; next, it was treated with hydrofluoric acid, washed with distilled water to neutral reaction, and then dried at 400 K. The residue after burning a purified G sample was 0.2 wt %.

Graphite was fluorinated in a nickel tubular reactor equipped with an external heater. The temperature was controlled with a chromel–alumel thermocouple. A G sample (2 g) in a nickel boat was placed inside the reactor; then, the reactor temperature was raised to 770 K, after which fluorine was admitted at 90 mL/min. Prior to use, fluorine was passed over NaF at 373 K to free it from HF. After filling the reactor with fluorine, the temperature was raised to 900 K at 0.16 K/s and maintained at this level for 1 h. After the synthesis was over, the sample was cooled to 298 K under a fluorine atmosphere. The resulting sample of fluorographite (FG) was a homogeneous white material with its particles conserving layered morphology; i.e., the average graphite particle size after fluorination remained practically unchanged (200–300 μm). X-ray powder diffraction did not show the G phase in the FG sample; the IR spectrum of the FG agreed with the literature [10, 11]. Chemical analysis showed 36.66 wt % C and 62.84 wt % F in the

Table 1. Characteristics and notations of test samples

Notation	Sample	Color	S_{sp}, m^2/g
G	Graphite	Black	0.6
FG	Fluorocarbon $(CF_{1.08})_n$	White	110
CF	Carbon fiber	Black	1.7
FCF	Fluorocarbon fiber $(CF)_n$	Light gray	320

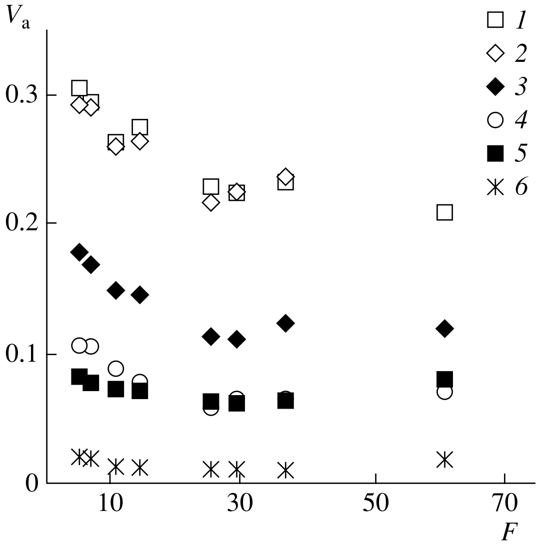

Fig. 1. Retention volume V_a (mL/m^2) at 403 K vs. carrier gas (helium) rate F (mL/min) on FG for (*1*) pentane, (*2*) butanol-1, (*3*) butanol-2, (*4*) 2-methylpropanol-1, (*5*) butane, and (*6*) 2-methylpropanol-2.

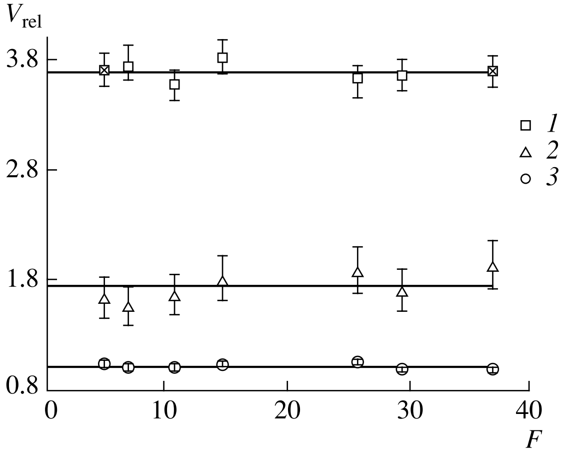

Fig. 2. Relative retention time V_{rel} at 403 K vs. carrier gas (helium) rate F (mL/min) on FG: (*1*) V_a(pentane)/V_a(butane), (*2*) V_a(butanol-2)/V_a(2-methylpropanol-1), and (*3*) V_a(pentane)/V_a(butanol-1).

product, which corresponds to the bulk formula $(CF_{1.08})_n$.

A sample of fluorinated carbon fiber (FCF) of composition $(CF)_n$ (as specified by the manufacturer) was prepared at the Research Institute for Electrocarbon (Elektrougli, Russia) by fluorinating viscose carbon fiber (CF) as in work [10]. Fluorinated carbon fiber is an unstructured powder, unlike carbon fiber (filaments ~300 μm in diameter). Therefore, for gas chromatography, an FCF sample was compacted under a pressure of 70 bar; then, the pellets were crushed and sieved to remove the 250–315 μm fraction. The specific surface area was determined by the Brunauer–Emmett–Teller technique from nitrogen adsorption isotherms at 77 K or by thermal nitrogen adsorption [12]. The procedure of gas chromatography experiments is described in [8, 12].

RESULTS AND DISCUSSION

Table 1 makes it clear that fluorination is accompanied by an almost 200-fold rise in the specific surface area S_{sp}. This significant change in S_{sp} as a result of fluorination can be due to the development of microporosity, the appearance of defects (e.g., microcracks in the starting carbon materials), and weakening of interparticle bonding [1, 11].

It is known [13] that for gas-chromatographic investigations of the surface properties of microporous adsorbent, it is important whether adsorption equilibrium is acquired under dynamic conditions [13]. The noninfluence of the carrier gas flow rate on the retention volumes is an argument in favor of the agreement of the measured retention volumes V_a (mL/m^2) and the Henry adsorption constants [13]. It is shown in the work that the V_a scatter around the mean value obtained on FCF does not exceed 3% over a fairly wide range of the rates from 2 to 10 mL/min. In view of the fact that good linear plots of $\ln V_a$ versus the number of carbon atoms in the molecules on FCF were obtained for *n*-alkanes from pentane to octane (with a correlation coefficient of 0.9999 at both 403 and 423 K), we may presume that the samples acquired adsorption equilibrium. Calorimetry [14] and gas chromatography support this presumption: the initial differential heat of adsorption of benzene on FCF is 44 kJ/mol at 373 K and 41 kJ/mol in the range 373–423 K.

Fluorinated graphite shows a general tendency toward an increase in V_a with decreasing helium flow rate (Fig. 1), which keeps us from regarding the measured V_a as thermodynamic constants. It is fairly likely that equilibration is hampered by the existence of micropores and ultramicropores in FG. It also should be taken into account that FG particles stick together during the gas-chromatographic experiment; as a result, the column permeability changes, and it is difficult to obtain precision data. However, relative retention volumes V_{rel} and retention indices I are comparatively little affected by the carrier gas rate. The scatter of the V_{rel} obtained on FG around the mean value does not exceed 3–11% in the range of the rates from 5 to 37 mL/min. By way of example, Fig. 2 displays V_{rel} versus F plots for three pairs of compounds. We may take that the retention parameters (I and V_a) obtained on FG qualitatively characterize the surface properties of FG and that they reflect intermolecular interactions in systems with FG. The retention parameters on FG hereafter mentioned in the text were measured at 29 mL/min.

Table 2 displays vapor retention volumes determined for several organic compounds (saturated or aromatic hydrocarbons, oxygenated or nitrogenated compounds). On fluorocarbons, a noticeable decrease is observed in V_a for all test compounds compared to the unfluorinated matrices; this observation agrees with the known data on the effect of carbon fluorination on nitrogen, methanol, and ethanol adsorption in the batch mode [3, 11].

On FG, V_a is 1.5–6 times that on fluorinated fiber. This agrees with the suggested existence of micropores and ultramicropores in the FG structure, which is known to enhance the energy of interaction with adsorbate molecules [13].

To evaluate the polarity of test samples, we employed an approach extensively used in gas chromatography; namely, we compared the Kovatz retention indices *I* of compounds capable of specific interactions (hydrogen bonding, electrostatic, and donor–acceptor interactions). Table 3 displays such data for the test materials and for graphitized thermal soot (GTS), which is classified as a reference apolar and chemically homogeneous adsorbent with a planar surface formed by the basal faces of graphite [13, 15]. In addition, *I* is only insignificantly affected by the temperature; e.g., on FCF at 373–423 K, the retention indices for the test compounds do not differ by more than 5 units. Similar inferences were derived previously from the investigation of the retention of oxygen-bearing compounds on GTS [16]. This allows us to compare the surface properties on the basis of *I* values determined at different temperatures.

The similar *I* values obtained for benzene and diethyl ether on G and GTS signify the chemical homogeneity of the graphite surface with respect to these compounds. However, for alcohols, acetonitrile, and nitromethane, *I* values on G are noticeably higher than on GTS. The main reason for the residual inhomogeneity of the G surface is the existence on graphite of prismatic faces bearing oxygenated functionalities, apart from the apolar basal face [15]. Molecules capable of strong specific interactions, including hydrogen bonding and donor–acceptor interactions [15], are mostly responsive to the presence of such groups. We cannot also rule out the existence of metal impurities on the G surface, which also can induce a noticeable rise in donor–acceptor interactions. Comparing *I* values obtained for different matrices, we see that the contribution of specific interactions during adsoprtion on carbon fiber is far higher than on G and the more so on GTS (Table 3). For example, *I* for alcohols on CF is at least 100 units higher than on G. For CF, one should account not only for the existence of adsorption active sites on its surface but also for the inhomogeneous CF structure, which consists of both textured carbon and various hybrid forms of amorphous carbon [1].

Fluorination abruptly decreases alcohol adsorption regardless of the type of carbon material. This effect indicates that the chemical homogeneity of the surface increases as a result of fluorination and is the manifestation of an increased hydrophobicity of the material. For benzene, diethyl ether, and acetone, the fluorination effect on the retention indices *I* on G is hardly noticeable, unlike on CF, which is due to the high chemical homogeneity of the matrix (Table 3).

Table 2. Retention volumes V_a (mL/m^2) for several compounds on graphite (G), fluorographite (FG), carbon fiber (CF), and fluorocarbon fiber (FCF) at 373* and 403 K

Adsorbate	G	FG	CF*	FCF*	FCF
Pentane	0.38	0.23	0.49	0.16	0.06
Hexane	1.46	0.96	1.71	0.49	0.16
Benzene	1.07	0.70	2.96	0.41	0.15
C_2H_5OH	0.24	0.02	0.92	0.022	0.01
Propanol-1	0.31	0.06	1.5	0.063	0.028
Propanol-2	0.18	0.03	0.89	0.048	0.022
Butanol-1	0.95	0.22	4.0	0.20	0.076
Diethyl ether	0.29	0.16	0.58	0.11	0.043
CH_3CN	0.24	0.03	0.6	0.03	0.02
CH_3NO_2	0.16	0.05	0.8	0.04	0.02

Table 3. Retention indices *I* on carbon fiber (CF), fluorocarbon fiber (FCF), graphite (G), fluorographite (FG), and graphitized thermal soot (GTS) [15, 16] at 373* and 403 K

Adsorbate	CF*	FCF*	G	FG	GTS
Benzene	641	589	579	579	572
Diethyl ether	514	464	475	471	461
Propanol-1	589	420	482	393	397
Propanol-2	548	395	438	347	381
Butanol-1	672	523	570	492	493
Butanol-2	–	499	549	445	470
2-Methylpropanol-1	–	498	541	398	466
2-Methylpropanol-2	–	455	482	271	422
Acetone	545	414	400	408	382
Acetonitrile	520	361	460	346	340
Nitromethane	538	398	427	388	340

Another conventional procedure for the characterization of the surface properties of solids is the comparison of the adsorption of *n*-alkanes and molecules having relatively similar weights and geometries but differing in their functionalities or π-bonds [13, 15]. Here, we demonstrated that over a wide temperature range, benzene is adsorbed on FG more weakly than hexane, diethyl ether is adsorbed more weakly than pentane, and butane and pentane are retained somewhat more strongly than propanol-1 and butanol-1, respectively (Fig. 3). One can see from Fig. 4 that similar results were obtained for FCF, although V_a for butanol-1 on FCF is slightly higher than for pentane. Similar tendencies in the adsorption of the test group of compounds were previously observed only for the most apolar, chemically homogeneous, and hydrophobic surfaces

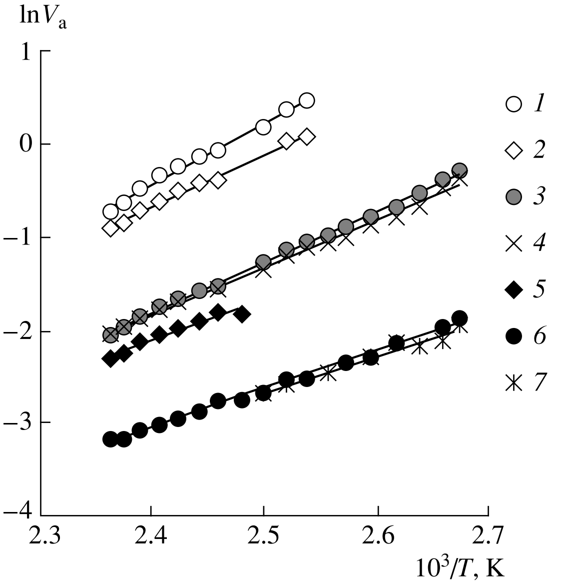

Fig. 3. ln V_a on FG vs. temperature for (*1*) hexane, (*2*) benzene, (*3*) pentane, (*4*) butanol-1, (*5*) diethyl ether, (*6*) butane, and (*7*) propanol-1.

such as hydrogen-treated GTS [15, 16]. Thus, we can infer from our results that fluorocarbons have surfaces adsorption on which is dominated by dispersion interactions, as on GTS.

Graphitized thermal soot is known as the irreplaceable adsorbent for separating structural isomers [13, 15]. The similarity of the chromatographic characteristics of fluorocarbons and GTS was the impetus for exploring the effect of the molecule geometry on the retention parameters in systems involving fluorocarbons; this was considered using propanol and butanol isomers as an example (Table 3). On the two fluorocarbons the retention parameters drop dramatically in going from linear to branched alcohols, which results from decreasing number of contacts between the molecule and the adsorbent surface. In the butanol group, the lowest *I* values were observed for the most heavily branched isomer (2-methylpropanol-2). Along with the common tendencies of alcohol adsorption, adsoprtion on fluorocarbons showed several unexpected features. On FCF, the difference between the retention of propanol or butanol isomers is approximately the same as on GTS; 2-methylpropanol-1 and butanol-2 are almost equally adsorbed on these two sorbents (Table 3). A different pattern is observed for FG (Table 3, Fig. 5). In this case, the adsorption of propanol-2 is one half that of propanol-1 (on FGF and GTS, some 1.3 times lower); the branched carbon skeleton of a 2-methylpropanol-1 molecule decreases the retention almost twofold compared to butanol-2 (where the hydroxide group moves to the position 2). In addition, for FG we observe an extremely weak adsorption of tertiary alcohol, which is retained more weakly than propanol-2 (Fig. 5). We encountered for the first time similar tendencies in the gas chromatography of isomeric alcohols on solids. These unusual properties of FG can be explained on the assumption that graphite fluorination yields a system of ultramicropores, which are poorly accessible to 2-methylpropanol-1 molecules with their branched carbon skeleton, and even less accessible to spheroid 2-methylpropanol-2 molecules. The retention features we revealed for FG might enable its successful application in gas chromatography of isomers, in particular, in wet assay, where high-hydrophobicity adsorbents are necessary.

On the whole, our results provide an argument in favor of the appropriateness of using fluorination for solving problems associated with the design of apolar,

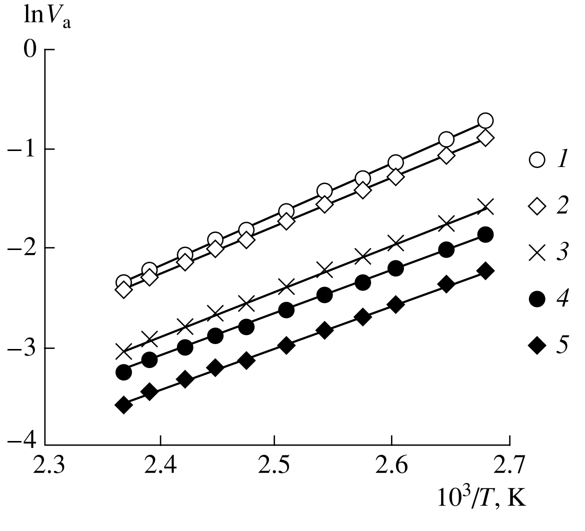

Fig. 4. ln V_a on FCF vs. temperature for (*1*) hexane, (*2*) benzene, (*3*) butanol-1, (*4*) pentane, and (*5*) diethyl ether.

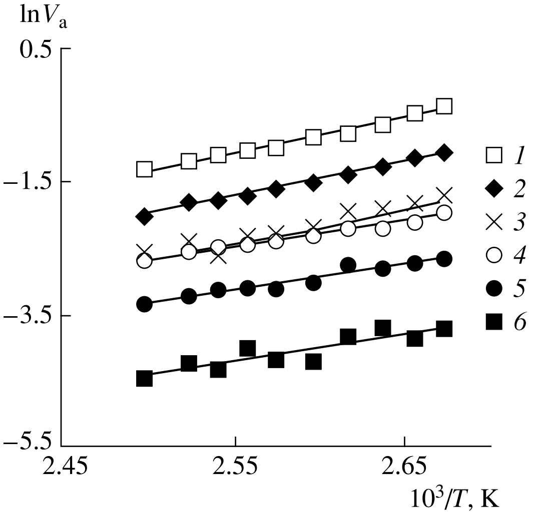

Fig. 5. ln V_a on FG vs. temperature for (*1*) butanol-1, (*2*) butanol-2, (*3*) 2-methylpropanol-1, (*4*) propanol-1, (*5*) propanol-2, and (*6*) 2-methylpropanol-2.

chemically homogeneous, and hydrophobic materials on the basis of fluorocarbons.

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