INTRODUCTION

An analysis of literature data on the chemistry of fluorinated carbons reveals a certain disproportion in our knowledge and its application. Indeed, on the one hand, we have developed routes to such compounds and a broad spectrum of their practical application [1–8] (that is, the production of cathodes of powerful chemical sources of electric energy, high-efficiency antifriction materials, catalyst carriers, thermally stable, as well as chemically and biologically inert coatings, and adsorbents for sample preparation and gas chromatography analysis). On the other hand, we have scarce information on their adsorption properties.

Although gas chromatography (which can provide data on the adsorption of a large number of test compounds over a wide temperature range) is among the most informative techniques of studying surface chemistry and the nature of intermolecular interactions [9], the potentialities of gas chromatography with respect to fluorocarbon materials have been used insufficiently. Unusual properties of fluorocarbons compared to known hydrophobic adsorbents include weaker adsorption of secondary alcohols than ketones, their dehydrogenation products. An analysis of the retention parameters of isomeric propanols and butanols revealed that the FCF surface is accessible to the adsorption of these molecules, and is mainly formed by planar homogeneous fragments. In contrast, the FG structure is porous; the pore width is comparable with the molecule size, which makes the adsorption equilibrium more difficult to reach.

EXPERIMENTAL

Fluorocarbon samples were prepared at the Research Institute of Electrocarbon Pieces (Elektrougli) and the Nikolaev Institute of Inorganic Chemistry of the Siberian Division of the Russian Academy of Sciences (Novosibirsk). According to the technical specification, the composition of the final products is \((\mathrm{CF}_x)_m\), where \(x \approx 1\). X-ray powder diffraction analysis [12] revealed that the interlayer distance for FCF and FG is 0.589 nm, which agrees with literature data [1, 3].

Fluorinated natural graphite (FG) was supplied as bright white scales (200–300 µm, specific surface area \(S_{sp} = 110 \text{ m}^2/\text{g}\)); fluorinated carbon fiber (FCF) was a light gray downy powder (\(S_{sp} = 320 \text{ m}^2/\text{g}\)) [10]. For gas chromatography, FCF samples were pressed under a pressure of 70 bar and the resulting pellets were ground, selecting a comparatively hard fraction of particles 250–315 µm in size.

IR spectra of FCF and FG samples as pellets with KBr (1 : 30 w/w) were recorded on a UR spectrophotometer as described in [13]. Before pressing into pellets, the samples were heated under nitrogen at 443 K for 10 h.
Gas chromatography measurements were carried out in a temperature range of 373 to 423 K on Khrom-5 and Tsvet 100 chromatographs (flame ionization detectors, nitrogen or helium as a carrier gas, glass columns 0.2–0.8 m in length and 1–3 mm in inner diameter). Prior to measurements, columns packed with the test samples were conditioned by passing helium or nitrogen at 443 K for 20 to 30 h. Compounds (0.1–0.2 ml) as vapor–air mixtures diluted 2 to 30 times were injected through a syringe. Retention times were measured with a stopwatch to within 0.1 s; the dead time was determined with a methane as a reference [13].

The retained volumes $V_a$ (ml/m$^2$), the Kovats retention indices, and the parameters $Q$ of the temperature dependences $\ln V_a = Q/RT + B$ (where $B$ is a constant) were determined from equations cited in [9, 13].

Karbopak SNT ($S_{sp} = 8.5$ m$^2$/g), an analog of graphitized thermal soot (GTS), was used as a model adsorbent.

RESULTS AND DISCUSSION

The IR spectra of fluorocarbons are shown in Fig. 1. The spectra of FG and FCF samples contain distinct absorption bands at 1220 and 1350 cm$^{-1}$ (curve 1) or at 1212 and 1328 cm$^{-1}$ (curve 2). They can be assigned to the CF stretching vibrations in the CF and CF$_2$ groups, respectively [14, 15]. The spectra of the fluorocarbons show virtually no absorption bands due to C–H vibrations. The spectra contain neither bands at 3200 to 3700 cm$^{-1}$ due to free or hydrogen-bonded OH groups nor bands at 1600 to 1800 cm$^{-1}$ due to carboxyl, hydroxy, and anhydride surface groups [16]. Therefore, the initial carbon matrices were virtually completely fluorinated and the resulting fluorocarbons bear no hydrophilic oxygen-containing surface sites. The same conclusion was drawn from data on the static adsorption of the water vapor: the limiting amounts of water adsorbed at FG and FCF exposed to the saturated water vapor at 298 K for seven days were only 0.10 and 0.16 µmol/m$^2$, respectively. This suggests the extremely high hydrophobicity of the test fluorocarbons.

At the same time, an analysis of the optical densities of the absorption bands due to the CF stretching vibrations in the CF and CF$_2$ groups (5.1 for FCF and 2.1 for FG) suggests that the number of CF$_2$ groups at the FG surface is higher than that at the FCF surface. This can account for different adsorption properties of these fluorocarbons.

In [10], it has been shown that fluorination of both carbon fiber and graphite substantially increases their $S_{sp}$ values (=200 times). This can be primarily associated with developed systems of micropores and mesopores in fluorocarbons. Indeed, according to a rough estimation using the Dubinin–Radushkevich equation [17], the effective $N_2$-based width of micropores is 1.6 nm for FG and 2.4 nm for FCF. This gives rise to a problem of determining the thermodynamic parameters under the conditions of gas chromatography. A necessary and supposedly sufficient prerequisite for the calculated retained volumes $V_a$ to equal the Henry constants is that $V_a$ should be independent of the flow rate $F$ of the carrier gas [9]. For the compounds adsorbed at FCF, the deviation of $V_a$ from the average was less than 3% upon a fivefold increase in the helium flow rate (Fig. 2). Therefore, the parameters obtained by gas chromatography for FCF can be considered thermodynamic constants. This conclusion is supported by close adsorption heats determined from GC and calorimetric data [18]: 26 and 22 kJ/mol for acetonitrile and 41 and 44 kJ/mol for benzene, respectively. However, $V_a$ appreciably increases at FG with a decrease in $F$ [10]; e.g., when $F$ was decreased 7.5 times from 37 ml/min, the retained volumes of ethyl methyl ketone and $n$-alkanes

![Fig. 1. IR spectra of (1) FG and (2) FCF.](image1)

![Fig. 2. Plots of the retained volumes $V_{rel}$ (ml/m$^2$) vs. the helium flow rate $F$ (ml/min) for FCF at 423 K: (1) pentane, (2) propan-1-ol, (3) propan-2-ol, (4) ethanol, and (5) methanol.](image2)