Gas-Chromatographic Studies of the Interaction between Water and Methanol Molecules and the Surface of Carbon Materials

YU. I. TARASEVICH, S.V. BONDARENKO AND A.I. ZHUKOVA
Institute of Colloid Chemistry and Chemistry of Water, Ukrainian National Academy of Sciences,
42 Vernadsky Avenue, Kyiv (Kiev) 03680, Ukraine
yuitaras@thomascat.kiev.ua

Abstract. The gas-chromatographic method is used to study the interaction of water and methanol molecules with active hydrophilic centres existing at the surface of thermally exfoliated graphite and graphitized thermal carbon black. The concentration of carboxyl and phenol hydroxyl groups at the surface of these sorbents is determined, and heats of adsorption of the studied molecules are shown to be $\bar{Q}_a = 40-39$ and $28-25$ kJ/mol, respectively. It is also shown that adsorption of water at the hydrophilic centres at lowest relative pressure values takes place with formation of clusters consisting of $n = 2$ water molecules.

Keywords: hydrophobic model sorbents, hydrophilic centres, carbon materials, water, methanol, adsorption isotherm, gas chromatography, interaction energy, cluster adsorption

Introduction

It is known (Kiselev, 1986; Patrykiejew, 1996) that carbon materials are extensively used as hydrophobic model sorbents in experimental and theoretical studies of the structure of adsorption layers and the energy of adsorbate-adsorbent interaction involving molecules of various nature. However, the presence of active hydrophilic centres, mainly the carboxyl and phenol hydroxyl groups, at the surface of carbon materials (Boehm, 1994), impedes such studies, if the adsorbates used represent substances with small polar molecules such as water or methanol. Therefore, it is important to determine the concentration of such centres and to develop the methods of their de-activation.

To determine the concentration of hydrophilic centres, an adsorption method was proposed where water was used as the adsorbate (Vartapetyan and Voloshchuk, 1995). However, certain doubts were expressed regarding the reliability of this method (Tarasevich, 2001a) in view of the ability of water molecules to be adsorbed at the hydrophilic centres with formation of clusters. Also, the sensitivity of the adsorption method, as applied to the water/graphitised carbon black system, is not sufficient enough to obtain

reliable adsorption data, especially in the region of low relative pressures (Brennan et al., 2001).

In this regard, it seems interesting to employ the gas-chromatographic method to determine the concentration of hydrophilic centres at the surface of nonporous carbon materials, and, at the same time, in addition to studies of the interaction of water molecules with such materials, to study also the interaction of methanol molecules, which are less capable for cluster formation at the surface, and exhibit a monomeric adsorption on the hydrophilic centres within the initial coverage region, i.e., each hydrophilic centre hosts only one methanol molecule (Tarasevich, 2001a; Tarasevich and Aksenenko, 2003). We address this topic in the present publication.

Experimental

The materials studied were: (i) the thermally exfoliated graphite (TEG) prepared by thermal treatment at 700°C of natural graphite which was enriched by its processing with a mixture of concentrated sulphuric acid and 30% hydrogen peroxide; and (ii) a graphitised thermal carbon black (GTCB) prepared by the

Table 1. Structural-adsorption characteristics of carbon adsorbents.

| Adsorbent | S, m^2/g | V_Σ, cm^3/g | Mesopores | |
			r, nm	V, cm^3/g
TEG	24	0.075	22.5	0.070
GTCB	54	0.414	17.5; 22.5	0.410

graphitising of ultra-disperse technical grade carbon at 2800°C.

To determine the structural-adsorption characteristics of the sorbents, the low temperature nitrogen adsorption at these surfaces was studied using ASAP 2000 M device (Micromeritics, USA) at −195°C (77.2 K); the samples were pre-evacuated at 120°C. The values of specific area S determined by the BET equation, the volumes V and radii r of mesopores, and the total volume of pores V_Σ of the sorbents are listed in Table 1. It is seen that V_Σ is only slightly higher than V, because the samples contain insignificant amount of micropores with volume smaller than 0.005 cm^3/g.

The texture of non-porous carbon adsorbents consists of stacked lamellar graphite particles. Large mesopores ($r = 17.5$–22.5 nm, cf. Table 1) characteristic of these materials are formed mainly by the gaps between adjacent lamellar particles. However, during thermal processing, a rolling of graphite particles can take place, which results in the formation of void tube-like structures with an internal radius $r \approx 25$ nm (Vartapetyan and Voloshchuk, 1995).

Noting the size and, especially, small volumes of micropores $V = 0.004$–0.005 cm^3/g, it could be argued that these micropores are in fact the nanosize micro-roughnesses of the TEG and GTCB particles surface (Tarasevich, 2001a). Such geometrical non-homogeneities of the sorbent particles are usually considered as relatively shallow micropores existing at the surface of mainly non-porous adsorbents (Dubinin, 1970; Tarasevich et al., 2001).

For these samples, the gas-chromatographic method was applied to obtain the elution peaks for water in the temperature range 62–94°C, and for methanol in the range 52–95°C. A Chrom−5 chromatograph (Czech Republic) was used; the steel columns (100 × 0.3 cm) were packed by the sorbent fraction 0.200–0.315 mm and stabilised prior to the experiment in the gas-carrier flow during 5–6 hours at 120°C.

An extremely important prerequisite to the studies of the interaction of water and methanol with carbon materials is the thermal pre-processing of the samples (Vartapetyan and Voloshchuk, 1995; Tarasevich et al., 1998; Kiselev and Yashin, 1967). In our experiments it was shown that pre-processing of the GTCB at 200°C resulted in the fact that no elution peaks were observed after the injection of first few portions of water into the column packed with the adsorbent, which indicates that at the initial stage the water molecules are chemisorbed by the sorbent. The surface-chemical reaction leads to decomposition of water molecules and to formation of surface-chemical compounds accompanied by emission of a large amount of heat (Tarasevich, 2001a; Tarasevich et al., 1998). First elution peaks that were observed at the adsorption values $a = 1.0$–1.5 μmol/g are essentially asymmetric, which prevents from determination of an accurate value of the isosteric adsorption heat. However, the estimates obtained in this way, $\bar{Q}_a \geq 45$ kJ/mol, are by about 5–8 kJ/mol higher than the values measured on the samples preheated at 120°C (see below). It could be supposed that these higher values of the adsorption heat, $\bar{Q}_a \sim 45$ kJ/mol, can be ascribed to the interaction of water molecules with surface radical groups (Tarasevich, 2001a). In view of these facts, for the main experiments, in which the gas-chromatographic studies of the interaction of water and methanol with the TEG and GTCB were performed, thermally at 120°C pre-processed samples were used.

The detection of methanol was performed using a flame-ionisation detector with nitrogen as carrier gas. For the detection of water a heat-conductivity detector was used; in this case helium was employed as carrier gas. Using the known procedures (Kiselev and Yashin, 1967), from the elution peaks the water and methanol adsorption isotherms were calculated in the relative pressure ranges p/p$_S$ = 0.001–0.200 and p/p$_S$ = 0.001–0.035, respectively. From these isotherms, the isosteres, i.e., lg(p) dependencies on 1/T for given constant amounts of the adsorbed substance a, were determined. The slope tg(β) of each isostere is equal to $-\bar{Q}_a/2.303$ R for this a value, where R is the gas constant. Finally, from this dependence, the differential isosteric adsorption heats were estimated as $\bar{Q}_a = -\text{tg}(\beta) \cdot 2.303$ R.

From initial sections of the methanol adsorption isotherms, using the Langmuir equation, we estimated the number of hydrophilic adsorption centres at the sorbent surface from the limiting adsorption value a$_\infty$, and the extent of the adsorption activity of the adsorbents – from the constant b. The concentration of hydrophilic

centres was determined as the ratio of a_∞ to the specific area S of the corresponding adsorbent.

Results and Discussion

Initial sections of water and methanol vapour adsorption isotherms obtained by the gas-chromatographic method at the GTCB surface were found to be convex with respect to the pressure axis for all temperatures, while for the TEG the isotherms were convex to this axis at 52 and 62°C. This latter fact should be ascribed to the interaction of polar molecules of the studied substances with active hydrophilic centres that exist at the surfaces of the adsorbents (Vartapetyan and Voloshchuk, 1995; Tarasevich, 2001a; Tarasevich et al., 1998). The adsorption isotherms of water and methanol vapours on the GTCB sample are shown in Figs. 1 and 2. The heats of water and methanol adsorption on the carbon adsorbents calculated from the isosteres (see Table 2), are close to the condensation heats of these substances at $\sim 65\,°C$, viz., L = 42.2 and 35.2 kJ/mol, respectively. This fact indicates that formation of hydrogen bonds takes place between water or methanol molecules and the active polar groups at the surface of the graphite particles.

The carboxyl groups are the pronounced hydrophilic centres of carbon sorbents (Boehm 1994; Brennan et al., 2001). These centres exhibit highest affinity with

Table 2. The dependence of the isosteric heats $\bar{Q}_a$(kJ/mol) of the water and methanol adsorption at the TEG and GTCB surfaces on the adsorption value a (μmol/g) in the temperature range of 52 to 95°C

a, μmol/g	Water		Methanol	
	TEG	GTCB	TEG	GTCB
0.5	–	–	39.3	41.0
1.0	39.2	39.7	35.6	37.5
1.5	–	–	33.1	34.2
2.0	33.6	35.5	29.2	32.2
2.5	–	–	26.6	28.4
3.0	28.7	28.9	23.7	26.1
3.5	–	–	21.6	25.0
4.0	28.9	28.6	21.5	24.5
5.0	28.1	28.3	–	–
6.0	27.5	28.0	–	–

respect to water molecules (Brennan et al., 2001). The initial isosteric heats of water and methanol adsorption at the GTCB and TEG surfaces measured at increased temperatures of the chromatographic experiment (see above) were $\bar{Q}_a \approx 40\,kJ/mol$, see Table 2. This value is close to the heats of water interaction with carboxyl groups of oxidised graphite and active coals, $\bar{Q}_a = 45\text{–}40\,kJ/mol$, which were obtained by adsorption and calorimetric studies at room
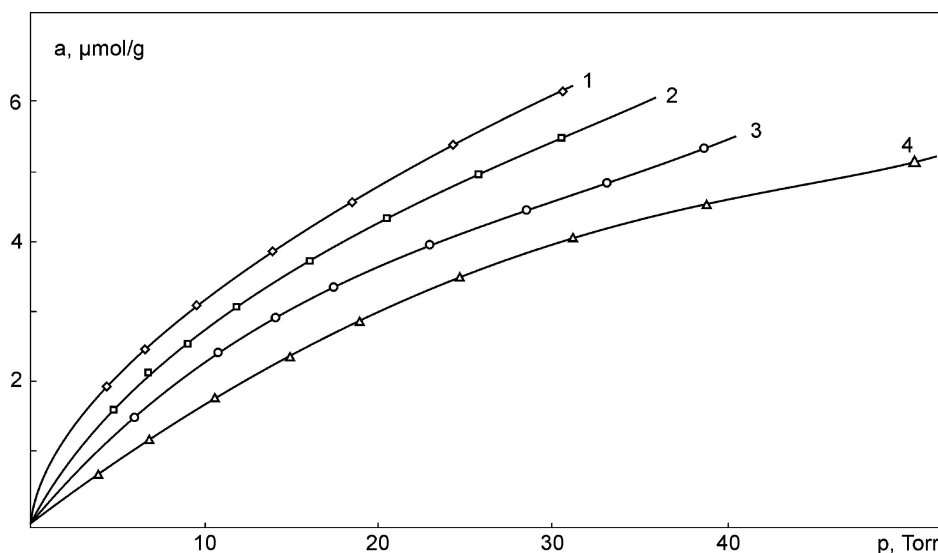

Figure 1. Initial sections of the isotherms for adsorption of water at graphitised thermal carbon black at the temperatures: 1, 65.3°C; 2, 72.0°C; 3, 82.0°C; 4, 93.9°C.
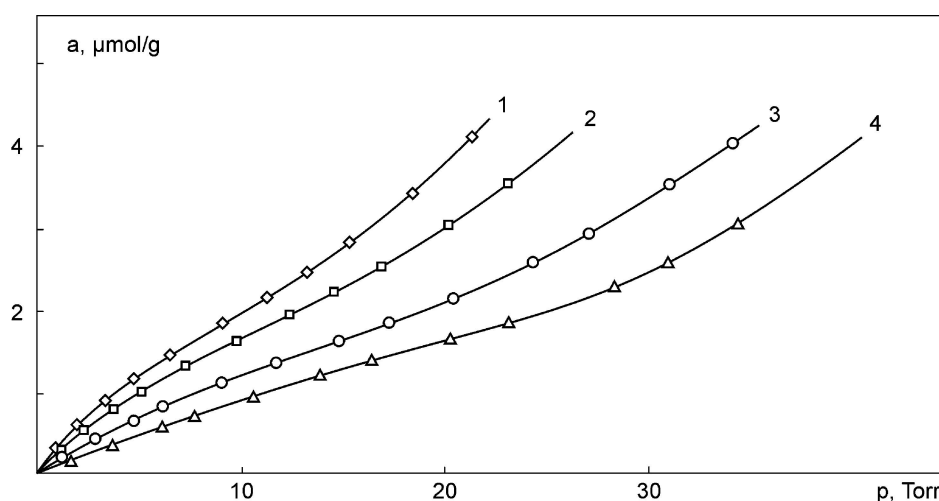
Figure 2.   Initial sections of the isotherms for adsorption of methanol at graphitised thermal carbon black at the temperatures: 1, 58.9°C; 2, 65.8°C; 3, 78.2°C; 4, 86.6°C.

temperature (Brennan et al., 2001; Vartapetyan et al., 1994).

It could be argued, therefore, that the initial adsorption of water and methanol molecules (adsorption values a = 1.0–2.0 μmol/g) takes place at the carboxyl groups of carbon materials. These groups are located at the side faces of the graphite particles and in the surface micropores of their basal faces. The methanol molecules located in these micropores are more susceptible to the influence of the 'walls' than the water molecules. Due to an additional van der Waals interaction between the methyl group of the methanol molecule and the carbon atoms located at the 'walls' of the surface micropore, the initial heat of the methanol adsorption $\bar{Q}_a$ = 41–37 kJ/mol (see Table 2) is higher than the condensation heat L = 35.2 kJ/mol.

For the adsorption values a = 3.0–6.0 μmol/g, the heats of adsorption of water and methanol on the carbon sorbents, $\bar{Q}_a \approx$ 28 kJ/mol (see Table 2), are essentially lower than the initial concentration values. This fact indicates that polar molecules interact predominantly with hydrophilic centres, which possess lower adsorption activity as compared to carboxyl groups. These hydrophilic centres are the phenolic hydroxyl groups which, similarly to the carboxyl groups, are the most common hydrophilic groups that exist at the surface of carbon materials (Boehm, 1994; Brennan et al., 2001; Kucher et al., 1980).

Water and methanol molecules simultaneously form two hydrogen bonds with the carboxyl groups of a

graphite surface: one bond is formed by the oxygen atom of the hydroxyl group, and another bond is formed by the hydrogen atom of the hydroxyl group of the adsorbed molecule (Tarasevich and Aksenenko, 2003). At the same time, these molecules form only one hydrogen bond with weakly acidic phenolic OH groups. It is quite natural, therefore, that the energy of interaction between small polar molecules with the phenolic OH centres of the graphite surface is essentially lower than the interaction with the carboxyl groups.

To estimate the concentration of these two main hydrophilic centres at the surface of studied sorbents, the initial portion of the methanol adsorption isotherms were processed in Langmuir equation coordinates. For this, the isotherms measured on TEG and GTCB at close temperatures, 52.2 and 58.9°C, respectively, were chosen. It was shown that in the Langmuir equation coordinates two linear sections of the isotherm exist, see, e.g. Fig. 3, characterised by different a_∞ and b values. The first section that corresponds to lower adsorption values and higher values of the energy-related coefficient b, characterises the interaction of individual methanol molecules with active surface carboxyl groups, while the second section characterises the gross adsorption of methanol on the carboxyl and phenolic groups. The amount of methanol adsorbed by phenolic OH groups was calculated from the difference between the limiting adsorption values characteristic of the two linear sections.
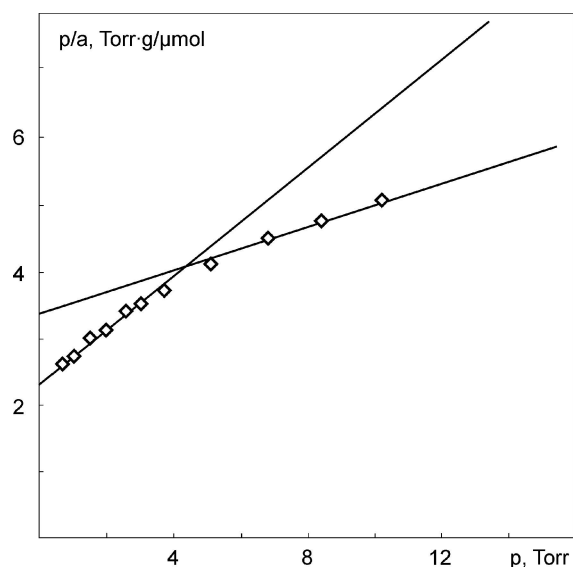
Figure 3. Adsorption isotherm for the methanol vapours at the graphitised thermal carbon black (58.9°C) in the Langmuir equation coordinates.

The methanol molecules are adsorbed individually ("monomerically") on the hydrophilic surface centres and do not form clusters; therefore, the number of active centres of both types is equal to the number of the methanol molecules adsorbed on these centres. The data summarised in Table 3 indicate that the value of the energy-related coefficient b which corresponds to the interaction of the methanol with the graphite carboxyl groups, is higher than that which corresponds to the interaction with phenolic OH groups. The total concentration of carboxyl and phenolic centres at the surface of the GTCB studied is $C = 0.068$ centres/nm^2, which agrees well with data reported in (Vartapetyan and Voloshchuk, 1995) where the total concentration of

acidic centres $C = 5.0\ \mu$mol/g $= 0.064$ centres/nm^2 was obtained for GTCB with a specific area $S = 47$ m^2/g, which was also prepared by graphitisation of ultra-disperse carbon.

At the surface of the TEG prepared from the natural material, the concentration of the phenolic hydroxyl groups is much higher than that at the GTCB surface, cf. Table 3. The increased concentration of phenolic OH groups is typical of the natural carbon materials (Kucher et al., 1980). This fact even was based upon by the hypothesis about a phenolic mechanism of oxidation of coals (Kucher et al., 1980).

The processing of the isotherms of water adsorption on the GTCB sample in the Langmuir equation coordinates (see Fig. 4) also shows that two energetically different sections exist, with the constants listed in Table 3. It is seen from Table 3 that the number of water molecules bound to carboxyl groups, 5.6 μmol/g, is 2.2 times higher than that of methanol molecules bound to these groups (2.5 μmol/g). For the phenolic groups, the corresponding values differ from each other by a factor of 2.5. This enables to suppose that at low coverages the adsorption of water molecules on the surface results in a cluster formation.

It was shown by quantum-chemical calculations (Tarasevich and Aksenenko, 2003) that the energies of the interaction of water and methanol molecules with
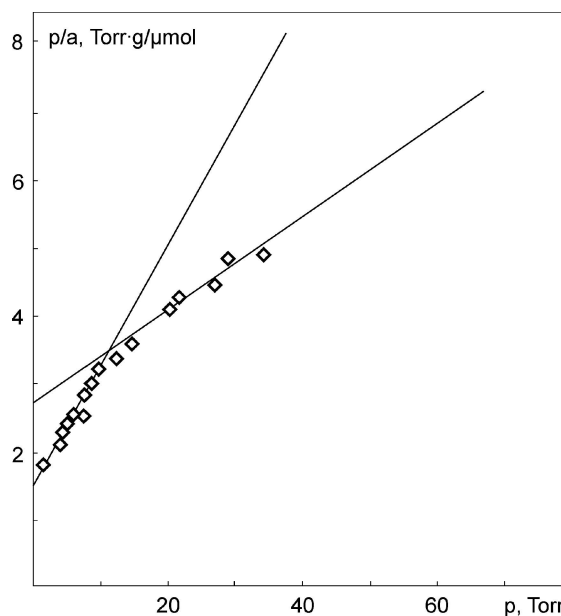
Table 3. The number a (μmol/g), concentration C (centres/nm^2) of active centres at the surface of carbon adsorbents and the energy-related parameter b (Torr^{-1}) for the adsorption of methanol and water at these surfaces

Sorbent	Carboxyl groups			Phenolic OH groups		
	a	C	b	a	C	b
	Methanol					
GTCB	2.5	0.028	0.17	3.6	0.040	0.05
TEG	2.9	0.073	0.14	7.1	0.180	0.03
	Water					
GTCB	5.6	0.062	0.12	9.0	0.100	0.025

Figure 4. Adsorption isotherm for the water vapours at the graphitised thermal carbon black (65.3°C) in the Langmuir equation coordinates.

the hydrophilic centres at the graphite surface are comparable to each other. Therefore, from a comparison of the values of water and methanol adsorption by the studied sorbents at similar heats of adsorption, and taking into account that, in contrast to water molecules, the methanol molecules are adsorbed individually at the centres, one can also estimate a number of water molecules which constitutes the adsorption cluster at the hydrophilic centre.

It follows from Table 2, that for the values $\bar{Q}_a =$ 39–40 kJ/mol the values of water and methanol adsorption are a(H_2O) = 1.0 μmol/g and a(CH_3OH) = 0.5 μmol/g. For adsorption heat values $\bar{Q}_a \approx$ 35 kJ/mol, these numbers are a(H_2O) = 2.0 μmol/g and a(CH_3OH) = 1.0 μmol/g. Therefore, the adsorption of water molecules at the carboxyl groups of carbon sorbents takes place with a formation of dimers, i.e. the number of molecules in the cluster is $n = 2$. For the heat values $\bar{Q}_a =$ 29–28 kJ/mol that are characteristic of the interaction of small polar molecules with phenolic hydroxyl groups, the adsorption values are a(H_2O) = 3–4 μmol/g and a(CH_3OH) = 2.5–2.0 μmol/g, i.e. $n = 2$–1.5.

The results presented above agree well with the data reported in literature. The value estimated by quantum-chemical calculations (Tarasevich and Aksenenko, 2003) for the graphite carboxyl groups is $n = 2$, while the adsorption experiment (Brennan, 2001) shows values of $n = 3$ for the carboxyl groups and $n = 1.5$ for the phenolic groups of carbon adsorbents. It follows from our adsorption-analytic data (Tarasevich, 2001b) that for the total set of acidic and basic centres at the surface of natural mesoporous coal at p/p$_S$ = 0.1 the value $n = 3.4$.

Conclusion

The data summarised above shows the applicability of the gas-chromatographic method for the determination of the concentration of active hydrophilic centres at the surface of non-porous carbon adsorbents, for the calculation of the heats of interaction of small polar molecules with these surfaces, and for the estimation of the number of water molecules which constitute the adsorption cluster.

Acknowledgments

References

Boehm, H.P., "Some Aspects of the Surface Chemistry of Carbon Blacks and Other Carbons," *Carbon*, **32**, 759–769 (1994).

Brennan, J.K., T.J. Bandosz, K.T. Thomson, and K.E. Gubbins, "Water in Porous Carbons," *Colloids and Surfaces A*, **187/188**, 539–568 (2001).

Dubinin, M. M., Surface and Porosity of Adsorbents, *Basic Problems in the Theory of Physical Adsorption*, M.M.Dubinin, V.V.Serpinskij (Eds.), pp. 251–269, Nauka, Moscow, 1970 (in Russian).

Kiselev, A.V., *Intermolecular Interactions in Adsorption and Chromatography*, Vysshaja Shkola, Moscow, 1986 (in Russian).

Kiselev, A.V., Ya.I. Yashin, *Gas-adsorption Chromatography*, Nauka, Moscow, 1967 (in Russian).

Kucher, R.V., V.A. Kompanets, and L.F. Butuzova, *Structure of Fossil Coals and their Ability for the Oxidation*, Naukova Dumka, Kyiv, 1980 (in Russian).

Patrykiejew, A., "Phase Transitions in Adsorbed Layers," *Adsorption on New and Modified Inorganic Sorbents*, A. Dabrowski and V.A. Tertykh (Eds.), pp. 599–627, Elsevier, Amsterdam, 1996.

Tarasevich, Yu.I., "Interaction of Water and Other Polar Substances with Various Adsorbents from Calorimetric and Chromatographic Data," *Teoreticheskaja i Eksperimentalnaja Khimija*, **37**, 199–215 (2001a) (in Russian).

Tarasevich, Yu.I., "Porous Structure and Adsorption Properties of Natural Porous Coal," *Colloids and Surfaces A*, **176**, 267–272 (2001b).

Tarasevich, Yu.I. and E.V. Aksenenko, "Interaction of Water, Methanol and Benzene Molecules with Hydrophilic Centres at a Partially Oxidised Model Graphite Surface," *Colloids and Surfaces A*, **215**, 285–291 (2003).

Tarasevich, Yu.I., A.I. Zhukova, E.V. Aksenenko, and S.V. Bondarenko, "Comprehensive study of Interaction of Water and other Polar Substances with Hydrophilic Centres on the Surface of Hydrophobic Adsorbents," *Fundam. of Adsorption 6*, F.Meunier (Ed.), pp. 81-86, Elsevier, Paris, 1998.

Tarasevich, Yu.I., A.I. Zhukova, E.V. Aksenenko, S.V. Bondarenko, O.V. Nazarenko, "Study of the Structure of a Surface-Porous Adsorbent using the Gas Chromatographic Version of the Molecular Probe Method," *Adsorption Sci. and Technol.*, **10**, 147–153 (2001).

Vartapetyan, R.Sh. and A.M. Voloshchuk, "Mechanism of Adsorption of Water Molecules at Carbon Adsorbents," *Uspekhi Khimiji*, **64**, 1055–1072 (1995) (in Russian).

Vartapetyan, R.Sh., A.M. Voloshchuk, A.A. Isirikyan, and N.S. Polyakov, "Hydrophobic-Hydrophilic Reversion of Graphitised Carbon Black," *Kolloidnyj Zhurnal*, **56**, 299–300 (1994) (in Russian).