Adsorption 11: 341–356, 2005

Adsorption and Mobility of Water and Benzene Molecules in Carbon and Polymer Adsorbents*

E.V. KHOZINA AND R. SH. VARTAPETYAN†
Institute of Physical Chemistry RAS, 119991, Moscow, Leninskii prospect, 31
vartapet@phyche.ac.ru

Abstract. The correlation between the adsorption and the mobility of adsorbed molecules was analyzed. The peculiarities of molecular mobility in microporous adsorbents with relatively rigid (active carbons) and non-rigid (polymer super-crosslinked and methacrylate sorbents) structure were studied using pulsed nuclear magnetic resonance (NMR) techniques. It was shown that the translational behavior of water and benzene in pores are connected with the specific adsorption mechanism. The NMR data allowed analyzing the changes of molecular state in the processes of adsorption. Diffusional properties of water molecules in the super-crosslinked polystyrenes and active carbons with relatively rigid framework are similar and differ from that in methacrylate polymer sorbents. Moreover, the results of NM relaxation measurements allowed analyzing the porous structure over the scale of pore sizes, while the scale of the self-diffusion measurements comprises the areas of different porosity. The NMR data agree well with the data of adsorption measurements and complement them.

Keywords: nuclear magnetic relaxation, self-diffusion, porous media, microporous adsorbents, adsorption mechanism, pore sizes, pore size distribution

Introduction

The distribution of pore sizes and the connectivity of pores are most important characteristics of porous solids, in particular microporous adsorbents. The pore sizes characterize adsorption capacity, the connectivity with the pore size distribution directly define the permeability of the porous media, heat- and electric conductivity, as well as the mass transfer processes. The sizes of micro- and mesopores of adsorbents are established, as a rule, from the analysis of the data of adsorption-desorption measurements, mercuric porosimetry and electron microscopy (Gregg and Sing, 1982; Karnaukhov, 1999; Fenelonov, 1995).

The correctness of the adsorption methods used for determination of the parameters of adsorbent porous structure is based on the knowledge of adsorption mechanism and the state of adsorbed molecules in pores. In particular the parameters of porous structure of carbon adsorbents are determined using the experimental adsorption isotherm for nitrogen vapor at 77 K or benzene at 293 K in the view of the known mechanism of adsorption (Gregg and Sing, 1982; Dubinin, 1982, 1983). The empirical dependence of the characteristic energy of adsorption on the pore sizes can be used to derive the micropore size distribution (Dubinin, 1983; Stoeckli et al., 1990).

In recent ten years, based on the studies of the mechanism of water vapor adsorption on porous and non-porous carbon adsorbents, the methods for estimation of micropore width (Vartapetyan and Voloshchuk, 1995) and mesopore surface of active carbons (AC) (Vartapetyan et al., 1995) from water adsorption were developed. The analysis of comparison plots is used with this purpose: the adsorption isotherms of water vapor adsorption in the AC under study are compared with that observed on the surface of non-porous graphitized carbon black (Vulkan-7H, graphitized at 2800°C), where unbound water clusters form and grow (Vartapetyan and Voloshchuk, 1995). Amount of

---

*Dedication: This work is devoted to memory of the professor W. Schirmer.

†To whom correspondence should be addressed.

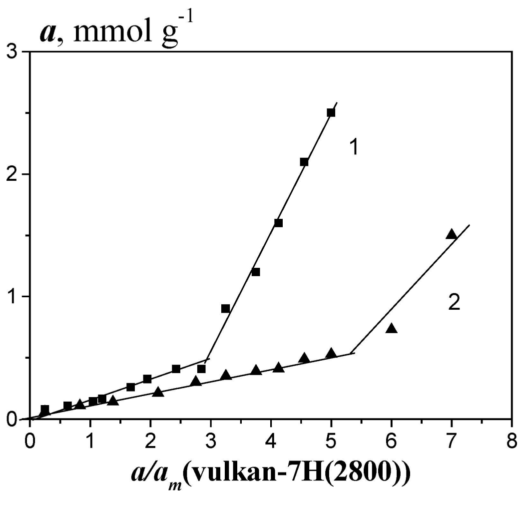


Figure 1. Comparison plots of the adsorption of water vapors for FAS-2 (1) and FAS-3 (2).

molecules in a cluster or amount of molecules per a single primary adsorption site (PAS) can be calculated as a ratio of the adsorption value, a, to the number of PAS, a_m. It occurred to be convenient to take the adsorption on the surface of graphitized carbon black expressed in the a/a_m units as abscissa, and the adsorption on the active carbon measured at the same relative pressures is used as the ordinate.

The comparison plots are straight lines from the coordinate origin. Their ordinates at $a/a_m = 1$ correspond to the number of PAS per 1 g of the AC and the inflection upward in the comparison plots of water vapor adsorption indicates on the onset of bridging between the molecules adsorbed on PAS located on the opposite walls of a micropore. The value of a/a_m at the inflection point in the comparison plots is related to the width, ***L***, of micropores (Vartapetyan and Voloshchuk, 1995). Figure 1 shows the example of the comparison plots for adsorption water vapors on the series of AC samples. (Fig. 1.)

It was found (Vartapetyan and Voloshchuk, 1995*)* that the heat of water adsorption on PASs in the area of low relative filling occurred to be less than the heat of water condensation (Vartapetyan et al., 1986, 1987; Dubinin et al., 1987). This is the main difference of water adsorption from the adsorption of nonpolar molecules such as benzene adsorbing on the surface or in pore volume of AC due to dispersion interactions (Dubinin, 1982, 1983) with the heat of benzene vapor adsorption always exceeding the heat of benzene condensation (Babaev et al., 1977).

The additional important information on a state of adsorbed molecules and properties of porous media can be given by the pulsed nuclear magnetic resonance (NMR) methods. In particular, the study of the processes of nuclear magnetic relaxation allows analyzing porous structure at the scale of pore, while the self-diffusion experiments are sensitive to a larger scale, covering ranges of different porosity.

Since the 70-s, the NMR methods with pulsed field gradient (PFG) have being used to investigate the mass transfer processes. The first who achieved considerable results in studying self-diffusion of adsorbed molecules in microporous adsorbents (zeolites) were Karger and Pfeifer (Karger, 1969; Pfeifer, 1976). The possibilities of NMR when applied to the investigation of the chemical state of the zeolite surface and to structure as well as to the mobility of adsorbed molecules, are reviewed in the article by Pfeifer (1976) and the monograph by Karger and Ruthven (1992).

The self-diffusion studies of water, benzene and methanol differing by their mechanism of adsorption on AC have been represented in a joint work performed by German and Russian scientists—Pfeifer, Karger, Dubinin, Voloshchuk, Vartapetian in the eighties (Vartapetian et al., 1985, 1989; Dubinin et al., 1988; Karger et al., 1989). In these works the average self-diffusion coefficients of adsorbed molecules at relative high fillings ($1 > \Theta > 0.2$) were measured.

Unlike active carbons, the polymer sorbents (PS), as a rule, have a non-rigid structure that varies its parameters in dependence on the chemical nature of adsorbed substances. In this connection, the determination of porous structure parameters by using the adsorption data of any standard substance (nitrogen, benzene), as performed in the case of practically non swollen carbon adsorbents has no sense.

This work observed the opportunities of NMR relaxation and self-diffusion measurements for determining the mobility of adsorbed molecules with different adsorption mechanism (water and benzene) and the pore structure parameters of microporous adsorbents with rigid (active carbons) and non-rigid (polymer adsorbents) framework.

Characteristics of the Samples

The nuclear magnetic relaxation and self-diffusion of water and benzene, adsorbed on the microporous samples of AC prepared from furfural with different degree of activation 1, 2, 3, and H, were studied. The

Table 1. The parameters of porous structure of AC under study calculated from the isotherms of nitrogen at 77 K and of water at 293 K.

	DR equation				DS equation			Analysis of the water adsorption isotherm		
AC	$S_{me}+S_g$ (m^2/g)	S_{me}, (m^2/g)	W_0 (cm^3/g)	**L** (nm)	W_0 (cm^3/g)	**L** (nm)	δ (nm)	S_{me} (m^2/g)	a_m (mmol/g)	**L** (nm)
1	1363	30	0.32	0.48	0.32	0.48	0.06	28	0.24	0.50
2	1029	120	1.20	1.32	0.62	1.34	0.30	150	0.15	1.30
3	2300[a]	–	–	–	–	–	–	360	0.13	1.80
	2100[b]			1.6[b]						
H	1154	80	0.58	1.08	0.61	1.20	0.28	95	0.28	1.08
SKT-6	1142	50	0.59	1.08	0.60	1.12	0.13	55	0.60	1.12

S_{me} – mesopore surface; S_g – geometric micropore surface area: $S_g = W_0/x_0$ (Dubinin, M.M., 1983); W_0 – micropore volume; **L** – the width of micropore for slitlike model; δ - the dispersion of the pore size distribution; a_m – the amount of primary adsorption sites for water adsorption – [a] calculated by the BET equation, [b] calculated by the comparison plots.

commercial sample SKT-6A has been also studied. The AC samples with the FAS trade mark produced by Neorganika Joint-Stock Co. (Elektrostal, Moscow Region, Russia), FAS-1, 2 and 3 are characterized by the virtually complete absence of ash admixtures as in the case of their industrial analog.

Table 1 contains the specific surface area (S_{BET}), the surface area of mesopores (S_{me}), the volume, (W_0) and the width (L) of a slitlike model of micropores and the dispersion (δ) of the micropore volume distribution of the AC samples under study. The parameters were calculated from the adsorption isotherms of nitrogen at 77 K according to the Dubinin-Radushkevich (DR) (Dubinin, 1975; 1982) and Dubinin-Stoeckli (DS) (Dubinin, 1983) equations and by the adsorption isotherms of water vapor (Vartapetyan and Voloshchuk, 1995). The pore width is connected to the adsorption energy by a Stoeckli ratio: $L = 10.8/(E_0\text{-}11.4)$ (Stoeckli et al., 1990).

As can be seen from the data in the Table 1, samples FAS-1 and FAS-2 with the micropore $L = 0.48$ and 1.32–1.34 nm, respectively, refer to a typical microporous AC. Sample FAS-2 is characterized by larger micropores, a broader size distribution of the micropores (parameter δ), and a larger mesopore surface. Note that FAS-1 contains mostly micropores, and that their mesopore surface area is relatively small.

According to Dubinin's classification, the FAS-3 sample with the pore width of 1.6–1.8 nm (depending on the estimation method) belongs to the supermicroporous active carbons. The Brunauer-Emmett-Teller (BET) equation and the comparison method for the estimation of the micropore parameters were used for an estimation of the porous structure parameters of sample FAS-3 (Michail et al., 1968).

The values of a_m and L (Vartapetyan and Voloshchuk, 1995), and the mesopore surface area S'_{me} (Vartapetyan et al., 1995) were determined from the adsorption isotherms of water. Assuming the uniform distribution of PAS over the surface, the distances between them were determined from a geometric micropore surface area S_g of the studied active carbons. The W_0 and L values were determined from the adsorption isotherms of nitrogen. Note that the parameters of porous structure of AC determined from the adsorption isotherms of nitrogen and water were similar.

The adsorption isotherms of water and benzene vapors on samples FAS-1 and FAS-2 at 293 K are presented in Fig. 2.

For easy comparison, the adsorption values are expressed in units of the adsorbate volume—W. In doing

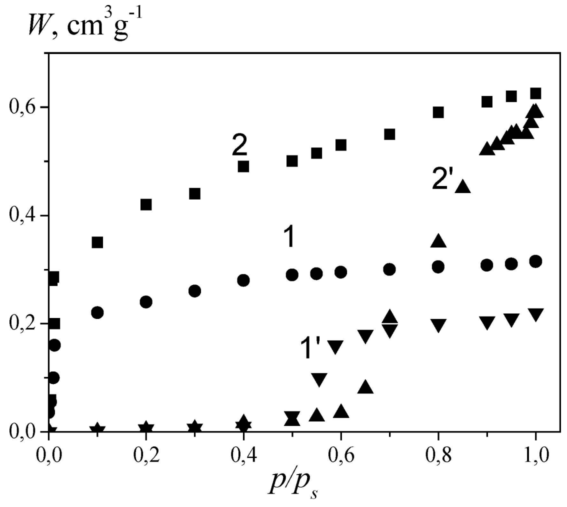


Figure 2. Adsorption isotherms of benzene (1, 2) and water (1′,2′) vapors for FAS-1 (1, 1′) and FAS-2 (2,2′) at T = 293 K.

so, the equal densities of the liquid and adsorbed states are assumed. Note that this assumption is fair for wide pores and small concentration of the initial adsorption sites.

The difference between the adsorption isotherms for benzene and water is due to the difference in the adsorption mechanism. The adsorption isotherms of water vapors on sample FAS-2 are described by more flat curves than those of sample FAS-1, indicating a broader pore distribution in sample FAS-2. The "tail" observed at $p/p_s > 0.95$ for the sample FAS-2 indicates a significant adsorption of water on the mesopore surface. Note the similar properties of the adsorption isotherm of water on FAS-3, but with a more noticeable "tail" and steepness compared with that for FAS-2. The maximum values of water adsorption, a_s, for the active carbons under the study FAS-1, -2, -3, -H are 13.3, 31.5, 48.5 and 41.6 mmol·g^{-1}, respectively.

The super cross-linked polystyrene "Styrosorb", MN-100 and MT-65 (Davankov and Tsyrupa, 1990) and the functionalized porous methacrylate polymer sorbents (Platonova et al., 1995) were considered as an example of those adsorbents that change their sizes during adsorption and have a non-rigid frame.

The sample MN-100, an industrial sorbent ("Purolite International Ltd.", UK), differs by the presence of amino groups in amounts of $0.2 \div 0.4$ mg-eq.units·g^{-1}. Another sample, MT-65, is a laboratory analog of an industrial sorbent of the same venture, MN-200. It contains no amino groups.

The parameters of porous structure of the polymer sorbents MN-100 and MT-65 as well as the amounts of PAS (a_m) and the maximum adsorption values for water vapors from the vapor phase (a_s) are listed in Table 2.

Figure 3 shows the adsorption isotherms of water on the PS under study and on AC for comparison. It is obvious that the adsorption isotherms of water on the PS and AC have the similar shape. The arched character of the adsorption isotherm at relative pressures $p/p_s \approx 0.6 \div 0.7$ indicates filling of the micropores of AC and PS by water.

Table 2. The parameters of porous structure of styrosorbs.

PS	S (m^2·g^{-1})	W (cm^3·g^{-1})	x_0 (nm)	a_m (mmol·g^{-1})	a_s (mmol·g^{-1})
MN-100	1000	0.5	0.9	0.13	11.5
MT-65	1050	–	0.8	0.13	19.1

S – specific pore surface, calculated from the BET equation, W – adsorption space calculated from the adsorption isotherm of n-pentane (Belyakova et al., 1996); a_m is calculated from the comparison plots (Vartapetyan and Voloshchuk, 1995).

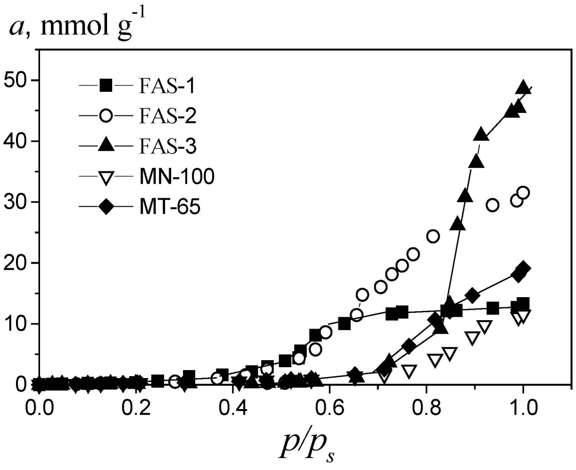


Figure 3. Adsorption isotherms of water vapors on active carbons and Styrosorbs at 293 K.

In spite of the presence of amino groups in MN-100 and of their absence in MT-65, the adsorption isotherms of water on MN-100 and MT-65 coincide at $p/p_s < 0.55$. That points to equal amounts of PAS in both polymer sorbents. It seems that amino groups in MN-100 are blocked by other groups and are inaccessible for water molecules in the vapor phase. The difference of the adsorption isotherm of water vapors on MN-100 and MT-65 at $p/p_s > 0.55$ is caused by their different adsorption volumes.

The AC and PS samples were filled with an adsorbate as follows. The sample with the solvent was evacuated in a thin-walled tube for 2 hours at 673 K in the case of AC sample and at 383 for PS and weighted. The samples were evacuated again and a specified amount of the substance was in injected using a microsyringe through the vacuum compression into an ampoule, which was preliminary placed in a Dewar flask with liquid nitrogen. Then the ampoule was sealed off, and the amount of the adsorbed substance was monitored by repeated weighting. The coverage (Θ) of microporous AC by the adsorbate is referred to the micropore volume found by analysis of the adsorption isotherm. The content of water or benzene adsorbed on the polymer sorbents, w, was calculated in mass %. The samples, completely saturated with water or benzene (with all pores filled), were prepared by introducing the liquid and removing the liquid excess by evaporation. The sealed ampoule was stored at 373 K for several hours to equalize the adsorbate concentration over the sample. After cooling, the ampoule was placed into the cell of an NMR spectrometer, where the temperature was kept constant.

All the measurements have been performed on an apparatus developed at the Chair of Molecular Physics of the Kazan State University (Maklakov et al., 1990).

The nuclear magnetic relaxation times were measured at the proton frequency 19 MHz. The spin-spin relaxation processes were examined by free induction decay (FID) signals, which followed the sequences of radio-frequency (RF) pulses $90_x{}^\circ - \tau — 90_y{}^\circ$—"solid-echo" (Levitt and Freeman, 1981). The PFG amplitude with duration of 10 μs was 0.1 T· m^{-1}. The time of recovery of the magnetic field uniformly did not exceed 10 μs. The Carr-Purcell-Meiboom-Gill (CPMG) sequence (Carr and Purcell, 1954; Meiboom and Gill, 1958) was used to determine the spin-spin relaxation time (T_2). The spin-lattice relaxation time (T_1) was measured using the sequence of RF pulses $(90_x{}^\circ - \tau_1 - 90_y{}^\circ - \tau_1 - 90_x{}^\circ - \tau_2 - 180^\circ - \tau_2)_n$ (Idiyatullin et al., 1990) which allows the measurement of the magnetization attenuation during "one passage". In this case, intervals of duration $\tau_1 = 10$ μs and $\tau_2 = 10$ ms between the RF pulses were used.

The observed multiexponential nuclear magnetization decays were approximated by a sum of exponential functions:

$$M(t) = \sum_i^N p_i \exp(-t/T_{1,2i}), \qquad (1)$$

where the number of addends, **N**, did not exceed three, p_i is the relative fraction of protons with a relaxation time $T_{1,2i}$. The correlation coefficient in the approximation was 97–98%.

The average T_2 values were determined using the equation:

$$1/T_{2av} = \sum_i^N p_i/T_{2i}\cdot \qquad (1a)$$

The measurements of nuclear magnetic relaxation were carried out at 303 K.

The PFG NMR measurements of the self-diffusion coefficients (SDC) of water and benzene were carried out at proton resonance frequency 60 MHz.

The self-diffusion coefficients were determined from an analysis of the amplitude of the spin-echo decay: the diffusional decay in the stimulated echo pulse sequences ($\pi/2 - \tau_1$-$\pi/2 - \tau_2 - \pi/2 - \tau_1-$ echo) (Stejscal and Tanner, 1965). The diffusion time, $t_d = \tau_1 + \tau_2$, was varied from 1.4 up to 312 ms. The maximum value of g was 50 T m^{-1}. The temperature was increased from 303 up to 333 K.

Results and Discussions

Nuclear Magnetic Relaxation of Water and Benzene Adsorbed on Active Carbons

The idea that the peculiarities of nuclear magnetic relaxation of molecules inserted into porous solids are determined by the geometry of the porous space is present practically in all theoretical models and their experimental verifications of recent times (Brownstein and Tarr, 1977, 1979; D'Orazio et al., 1989; Hills and Snaar, 1995; Kleinberg et al., 1994; Godefroy et al. 2001). The nuclear magnetic relaxation of a molecule in a pore volume is determined by its interaction with surrounding similar molecules. The corresponding relaxation time is T_b. Near the surface of pore walls or in a surface layer of thickness λ, nuclear magnetic relaxation occurs on the so-called surface sinks of nuclear magnetization (surface functional groups, lattice defects, etc.) (Brownstein and Tarr, 1977), with the corresponding time T_s. Due to collisions with immovable or slowly-moving particles, relaxation occurs much more rapidly than in the volume, $T_s << T_b$ (condition of nuclear relaxation acceleration near the surface).

If a substance introduced into a pore does not form chemical bonds with the pore surface, the thermal motion (self-diffusion) induces exchange between molecules in the surface layer and on the pore volume. Under conditions of fast diffusion, when the relaxation time of a molecule in the pore considerably exceeds the time needed for the molecule to cover distances comparable with the pore size, the relaxation of a molecule in the pore is characterized by a single relaxation time (Brownstein and Tarr, 1977, 1979). The value of this time is proportional to the characteristic pore size, x, viz., the ratio of the pore volume V to the surface S:

$$T_{1,2} = \frac{V}{\mu S} \sim x, \qquad (2)$$

where μ is the so-called surface relaxation strength or the density of surface sinks of magnetization. The parameter μ can be formally defined as (D'Orazio et al., 1989):

$$\mu = \lambda / T_s.$$

The relation (2) served as a basis for the analysis of nuclear magnetic relaxation measurements in different porous materials, in particular in model porous glasses (Hills and Snaar, 1995).

For proper estimation of pore sizes according the proposed algorithm it is necessary to have all information about the parameter of surface relaxation strength. The study of the mechanism of surface relaxation (Kleinberg et al., 1994) resulted in the following equation for the relaxation of the liquid in one pore:

$$\mu_1 = \frac{n_m \lambda}{T_{1m} + \tau_m}, \quad \mu_2 = \frac{n_m \lambda}{T_{2m}}, \tag{3}$$

Where n_m is the relative fraction of the surface occupied by paramagnetic ions; T_{1m} and T_{2m} are, respectively, the times of spin-lattice and spin-spin relaxations of molecules interacting with paramagnetic ions, τ_m is the lifetime of liquid molecule in the coordination complex, and $\mu_{1,2}$—are the parameters of surface spin-lattice and spin-spin relaxation strength, respectively.

All mentioned works considered nuclear magnetic relaxation of liquid molecules in macro- and mesoporous solids. Here, we are going to present the peculiarities of nuclear magnetic relaxation of adsorbed molecules in microporous adsorbents.

As a rule, active carbons as well as polymer adsorbent particles contain H atoms entering the composition of compounds chemically bound to the surface or belonging to the AC structure. It has been found that the FID signal observed in water (benzene)-AC systems is a sum of two functions. The applying of the modified Goldman-Shen sequences to the systems under study found that the fast decaying component in FID corresponds to protons that belong to AC (Khozina et al., 2002). The applying of Carr-Purcell-Meiboom-Gill (CPMG) pulse sequence extracted this component.

Figure 4 shows the decay of transverse nuclear magnetization in benzene adsorbed on FAS-2 resulted after the application of CPMG sequence with $\tau = 100\ \mu$s.

The observed signal was approximated by the sum of two exponentials with relaxation times $T_{2\min}$ and $T_{2\max}$:

$$M(t) = p_1 \exp(-t/T_{2\min}) + p_2 \exp(-t/T_{2\max}),$$
$$p_1 + p_2 = 1 \tag{4}$$

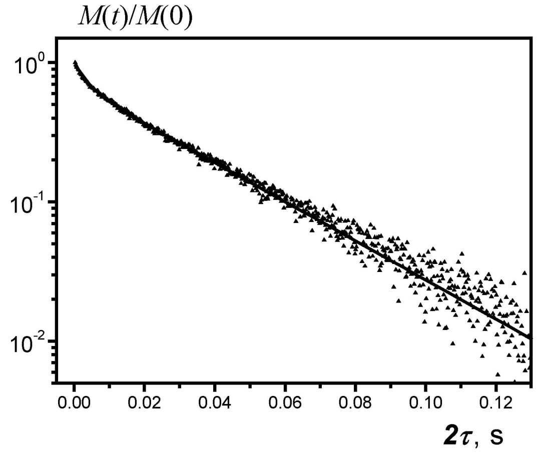


Figure 4. Decay of the transverse magnetization in FAS-2-benzene at $\Theta = 0.6$ resulting from the application of the CPMG pulse sequence (the interval between the π-pulses is 100 μs at 303 K. The solid line is the approximation of the attenuation by the sum of two exponentials with relaxation times $T_{2\min}$ and $T_{2\max}$.

where $p_{1,2}$ are the relative fraction of protons with the corresponding relaxation times.

According to Brownstein—Tarr theory, nuclear magnetic relaxation of a molecule in a pore is characterized by a single relaxation time T_1 or T_2, defined by Eq. (2).

Therefore, the observed distribution of relaxation times is defined by the pore size distribution:

$$P(T_{1,2i}) \to P(x_i) \tag{5}$$

In addition, the areas of large and small pores are divided in space. In opposite case, when they are mixed, the relaxation is described by an averaged relaxation time (D'Orazio et al., 1989).

Thus, a proportion based on Eq. (2) for each adsorption system with specified benzene or water loadings of pores is obtained:

$$\frac{T_{2\max}}{x_{\max}} = \frac{T_{2\min}}{x_{\min}}. \tag{6}$$

The size of least pores, $x_{\min}$, where benzene or water molecules could be find, were assumed to be no less their sizes, i.e. 0.3 nm for water and 0.37 nm for benzene.

The largest size of micropores in AC, where benzene or water molecules were adsorbed, $x_{\max}$, were calculated using Eq. (6) to be equal 1.4, 3.2 and 2.2 nm in FAS-1, -2, -3, correspondingly. The broadest pore size

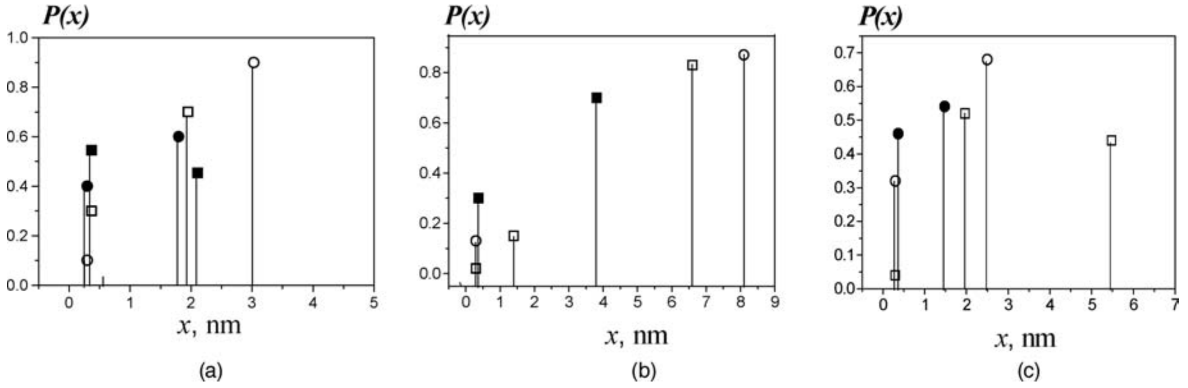


Figure 5. The water and benzene distribution over pores of FAS-1(a) defined from T_2 data for benzene at $\Theta = 0.05$, (●)1 (■) and for water at $\Theta = 0.05$ (□), 0,89 (○); in FAS-2 (b) at $\Theta = 0.6$ (■ – benzene, □ – water) and in FAS-2 saturated by water (○); in FAS-3 (c) at $\Theta = 0.1$ (● – benzene, ○ – water) and 1 (□ – water) at $T = 303$ K.

distribution was observed in FAS-2 system (T_2 varied from 3.5 ms to 31.0 ms.). This conclusion agreed with the data obtained from nitrogen and water adsorption (see Table 1)

Thus, the distribution of the relaxation time $P(T_2)$ was used to find the relative fraction of molecules over pores of one or another size, i.e., estimate the pore size distribution $P(x)$ (Fig. 5).

The comparison of $P(x)$ for water and benzene in FAS-1, 2, 3 indicated that FAS-1 disposes of the largest fraction of micropores ($x \leq 2.1$ nm) within the total pore volume. At the same time, FAS-2 is characterized by the broadest pore size distribution. According the adsorption data, benzene is predominantly adsorbed in micropores, while the water adsorption is determined by the presence of PAS.

As follows from Eq. (3) the parameter of the surface relaxation strength in macro- and mesoporous solids is a linear function of the relative fraction of the surface occupied by paramagnetic ions, n_m. Hence, for micropores we can suppose the similar dependence between μ and the volume concentration of PAS, i.e. the parameter (a_m/W_0). It is reasonable to consider that the average spin-spin relaxation time T_{2av} of adsorbed water at complete micropore saturation is determined by the average density of the sinks of nuclear magnetization all over the sample. Figure 6 presents the dependence T_{2av} at complete micropore saturation on the volume density of PAS (a_m/W_0) for various AC. We added to the data for SKT-6, which is commercial active carbon. In contrast to AC of FAS type SKT is characterized by a greater value of a_m while the pore sizes and the micropore volume are the same as in FAS-H and FAS-2 (see Table 1). The linear feature of the observed dependence $T_2 = f(a_m/W_0)$ indicates the dominant role of the PAS as sinks of nuclear magnetization of the adsorbed water.

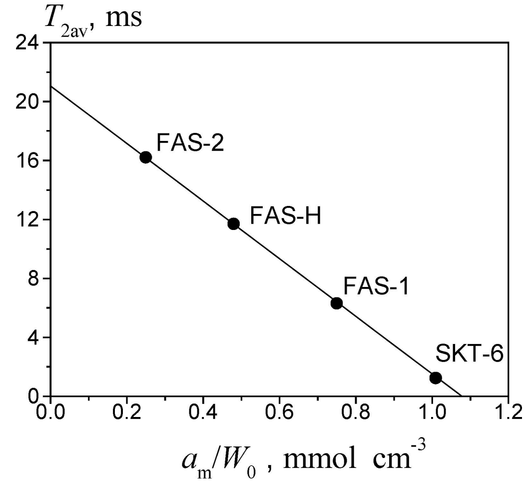


Figure 6. Dependence of the T_{2av} values of water on the volume density of PAS, a_m/W_0, for FAS-1, FAS-2, FAS-H and SKT-6.

In our approach, two assumptions were made. The first is that the PAS distribution (sinks of nuclear magnetization) over the adsorbent pore volume is uniform. The second assumption is an uncertainty of the smallest pore size corresponding to $T_{1,2\min}$. We assume for water molecule $x_{\min} = 0.30$ nm, an average value over the molecule size range from different authors (Ainscough and Dollimore, 1987) and $x_{\min} = 0.37$ nm for benzene. The latter is a thickness of benzene ring (Gregg and Sing, 1982).

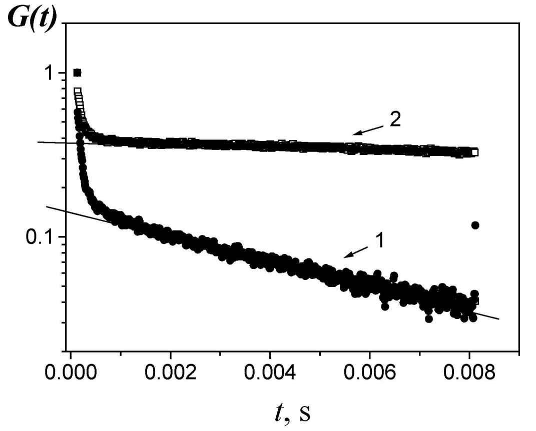


Figure 7. FID signal in the adsorption systems MN-100—water (1) and MT-65—water (2) for $w = 0.1$ at 303 K. The straight lines define the exponential components with $T_{2\min} = 3$ ms (MN-100) and 0.6 ms (MT-65) and the corresponding relative fraction $p = 0.46$ (MN-100) and 0.22 (MT-65) resulting from the approximation by Eq. (9).

Nuclear Magnetic Relaxation of Water and Benzene Adsorbed on Polymer Adsorbents

The free induction decay (FID) of water adsorbed in the pores of MN-100 and MN-65 for relative mass content $w = 0.1$ are presented in Fig. 7.

The FID in the adsorption systems PS−water (benzene) were approximated by a sum of three components:

$$G(t) = p_1 \exp(-t^2 W_2/2) + p_2 \exp(-t/T_{2\min}) + p_3 \exp(-t/T_{2\max}), \qquad (7)$$

It followed from the measurement of the FID in the dried sample of PS that the component of the FID described by a Gaussian (first term in Eq. (7)) reflects the relaxation of the "structural" protons of PS. The other components were approximated by exponential functions. The obtained values $T_{2\min}$ and $T_{2\max}$ describe the relaxation of the adsorbed molecules.

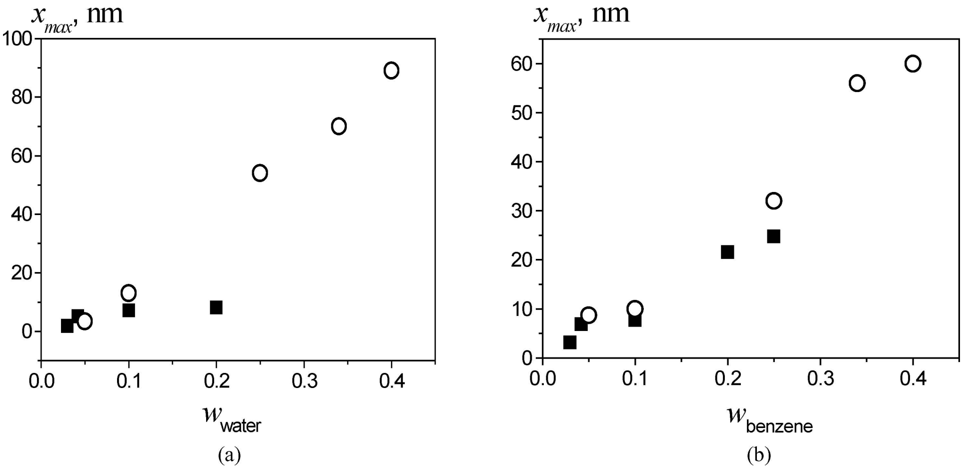
Note that the values of $T_{2\min} \sim 10^{-5}$ s occurred to be less than $1/|\gamma\ \Delta H|$ and could be defined from the FID signals directly. The CPMG experiments were used for more exact measurements of the $T_{2\max}$ values that notably exceed $1 / |\gamma\ \Delta H|$.

Since the passage time of water or benzene over distances of the pore size are smaller than $T_{2\min} \sim 10^{-5}$ s, the conditions the fast diffusion is fulfilled for the adsorption systems PS − water (benzene). Hence, in accordance with Brownstein-Tarr theory the equation (6) also occurs to be valid. Again it is possible to estimate the value $x_{\max}$.

Figures 8(a) and (b) show $x_{\max}$ as a function of the adsorbate content for water (a) and benzene (b) in MN-100 and MT-65.

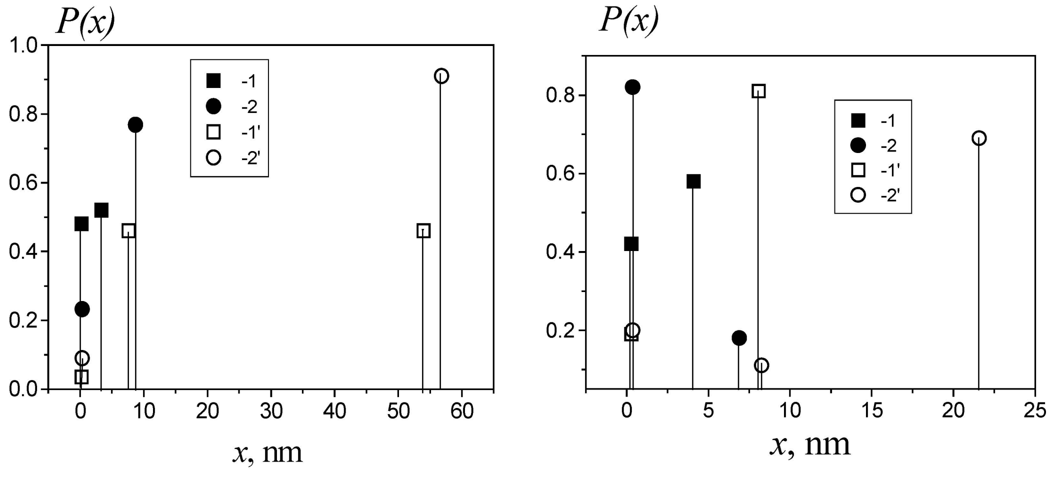
It is obvious that for both water and benzene, the values $x_{\max}$(MT-65) are close to $x_{\max}$(MN-100) for low content (up to $w \sim 0.2$) and exceed $x_{\max}$(MN-100) for higher w. The observed distributions of the spin-spin relaxation times of water or benzene in PS indicate the existence of areas of different porosities in MN-100 and MT-65.

Figures 9a and b shows the pore size distribution functions, $P(x)$, determined the spin-spin relaxation measurements. The data are presented for low and large



(a) (b)

Figure 8. (a, b) Dependence of the largest pore size in MN-100 (■) and MT-65 (○), filled by water (a) and benzene (b) on the mass content of the adsorbate (water, benzene) at T = 303 K.



(a)

(b)

Figure 9. (a, b) Distribution of water (1, 1′) and benzene (2, 2′) molecules over pores with specific sizes in the samples MT-65 (a) and MN-100 (b) at different mass content of adsorbate: 1, 2—$w = 0.05$, 1′, 2′—$w = 0.34$ (a) and 1, 2—$w = 0.03$; 1′, 2′–$w = 0.20$ (b), calculated from the nuclear magnetic relaxation data at $T = 303$ K.

contents of adsorbate. It is obvious that the interval of the filled pores of MT-65 (0.3 nm $\leq x <$ 60 nm) is broader than in MN-100 (0.3 nm $\leq x <$ 25 nm). This indicates the wider pore size distribution in MT-65.

It is significant to note some peculiarities of the adsorption of benzene and water in the PS under study. As it follows from Fig. 9 (a) and (b), the benzene molecules are adsorbed in the wider pores of MT-65 and MN-100. For example, compare the values $x_{\max} = 56$ nm (MT-65) and $x_{\max} = 21.7$ nm (MN-100) for benzene with those for water: $x_{\max} = 54$ nm (MT-65) and 7.5 nm (MN-100) at equal content $w = 0.34$ (MT-65) and 0.2 (MN-100). One can suppose that this adsorption behavior of benzene is caused by the so-called adsorption deformation which is significant for benzene in comparison with water.

The observed behavior is in contrast with the adsorption of water and benzene on AC indicating a distinct difference between the adsorption properties of AC with a rigid framework and of the deformable PS.

Self-Diffusion of Water and Benzene Molecules Adsorbed on AC.

In pure liquids (water or benzene) the dependence of the logarithm of the spin-echo amplitude on the square of the pulse field gradient $A(g^2)$ is linear and corresponds to the expression for diffusion decay due to Brownian diffusion in a one-phase system with a single SDC and a single value of relaxation time (Stejscal and Tanner, 1965):

$$A(g^2) = A_0 \exp(-(\gamma g \delta)^2 t_d D), \tag{8}$$

where$A_0 = \exp(-\frac{2\tau_1}{T_2} - \frac{\tau_2}{T_1})$ for the case of an exponential relaxation, γ, δ and g denote the gyromagnetic ratio, the duration and the amplitude of the gradient pulses. The parameter D is the self-diffusion coefficient (SDC) of the molecules under study.

The opportunities of self-diffusion measurements for investigation of porous media are described (Stallmach and Karger, 1999).

Figure 10 represents the diffusion decays of the spin-echo, $A(g^2)$, for water in pores of FAS-1 and FAS-3 at different fillings, Θ.

It is obvious that the observed diffusion decays (DD) deflect from the exponential behavior corresponding to Eq. (8). The diffusion of molecules in microporous media corresponds to the case when all molecules undergo collisions with pore walls during observation time. In the case of a homogeneous and isotropic porous sample, the average propagator of molecular motion is described by a Gaussian (Stallmach and Karger, 1999). The corresponding diffusion decay of the spin-echo is described by Eq. (8) with the effective SDC determined by the porosity of the sample.

The above presented data of nuclear magnetic relaxation indicate the existence of areas of differing

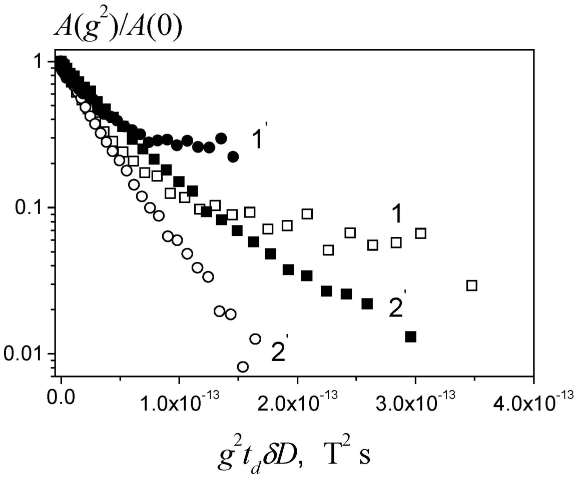


Figure 10. Diffusion spin-echo decays $A(g^2)/A(0)$ of water in pores of FAS-1 (curves 1, 2) and FAS-3 ($1'$, $2'$) at the filling degrees $\Theta = 0.06$ (1); 0,89 (2); 0.02 ($1'$) and 1 ($2'$). The diffusion time $t_d = 4$ ms.

porosities in the AC under study. Hence, the multiexponential DD reflects the multiphase system (Karger and Ruthven, 1992, D.M.; Maklakov et al., 1990). Assuming that the propagator in each phase is a Gaussian for a multiphase system, the diffusion decay can be presented as a sum of exponential terms (Eq. (8)) with a certain SDC. Each phase has a set of relaxation times and self-diffusion coefficient. If the number of phases is more than 4, the diffusional spin-echo decays are described by a spectrum of SDC:

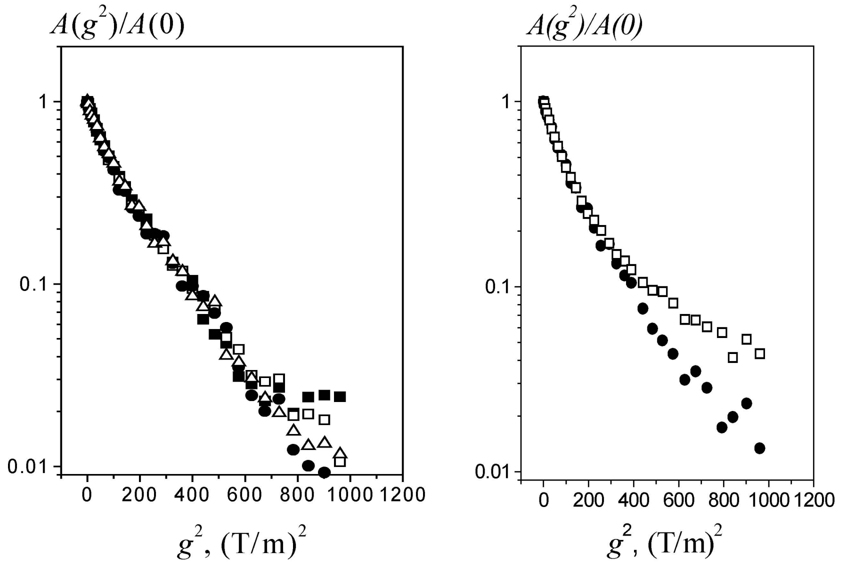
$$A(g^2)/A(0) = \int p(D)[\exp(-\gamma^2\delta^2 g^2 t_d D)]dD \quad (9)$$

The width of spectrum, $\ln^2\sigma$, is defined using the log-normal distribution $p\,(\,D)$ of diffusivities:

$$p(D) = \frac{1}{\sqrt{2\pi}\,\ln^2\sigma}\exp\left(-\frac{\ln^2(D/D_{av})}{2\ln^2\sigma}\right)$$

where σ is the width parameter of the SDC spectrum and D_{av} is the average SDC determined from the slope of the tangent to the initial ($g\rightarrow 0$) part of the DD.

Note, the existence the areas of different porosities in AC was indicated by the multiexponential relaxation. We assume that the multiexponential diffusion decays are caused by the existence of the areas of different porosities and spatial distribution of adsorbed molecules. The exchange processes between these areas would lead to the exponential DD as the diffusion time is increased with the mean value of the SDC being constant. The exchange processes can be found from the examinations of DD at different diffusion times. Figure 11(a) and (b) represents the DD in FAS-3



(a)

(b)

Figure 11. Diffusion spin-echo decays for FAS- 3 saturated by water (a) and benzene (b), observed at different diffusion times, a: $t_d = 1.4$ ms (●), 5 (□), 120 (■) and 300 ms (△); b: $t_d = 1.4$ (□) and 326 ms (●) for $t_d\delta^2 = \text{const}$ at 303 K.

saturated by water (a) and by benzene (b) observed at different values of t_d.

The SDC distribution of water in FAS-3 was rather narrow ($\sigma = 0.15$) and didn't depend on $\mathbf{t}_d$ in the interval from 1.4 to 326 ms (Fig. 11(a)). Hence, fast exchange leads to an averaging over the diffusivity distribution for $t_d < 1.4$ ms. Using the Einstein relationship with D_{av} for water and $t_d = 1.4$ ms, the extension of FAS-3 pores filled by water characterized by a single SDC, l, one obtained: $l \sim 3\,\mu$m.

When investigating the dependence of diffusion decays on t_d in the FAS-3- benzene sample for $\Theta = 1$, a change in the width of the SDC spectrum with the increase of t_d was observed (see Fig. 11(b)): the value σ decreases from 0.41 to 0.19 with t_d increasing from 5 to 326 ms. The unchanged average SDC for different values of t_d excludes that the observed changes of DD are caused by the relaxation influences. Therefore, molecular exchange between regions with different diffusivities in FAS-3 occurs at a much slower rate. The further increase of the diffusion time up to 400 ms does not reveal any changes in the DD shape. Using the Einstein relation for the SDC of benzene and $t_d = 326$ ms one can estimate the dimension of the heterogeneity in the adsorption system FAS-3-benzene to be $l \approx 32\,\mu$m.

Studies of molecular mobility in microporous systems testified that the measured diffusivities are defined not only by the geometry of the porous space but also by the interaction with the pore walls (Karger and Ruthven, 1992). Thus, for an analysis of the obtained values of the dimensions of heterogeneities of the adsorption systems the peculiarities for adsorption mechanism must be taken into account. Hence, differences between the values obtained with water and benzene in FAS-3 indicate differences with spatial distribution of benzene and water in FAS-3, caused by their different adsorption properties. The regions of heterogeneity in FAS-3−benzene correspond to the zones of different porosities in FAS-3, and the exchange between these zones is hampered. Previous studies organic substances in AC-72, which is close by its origin to FAS-3, revealed microporous zones of large dimensions up to 100 μm (Karger et al., 1989).

As follows from Fig. 10, in FAS-1, 2, 3 at water loading $\Theta < 0.09$, the DD (curves 2 and 4) results a sum of two exponents:

$$\begin{aligned} A(g^2)/A(0) &= p_1 \exp(-\gamma^2\delta^2 g^2 t_d D_1) \\ &\quad + p_2 \exp(-\gamma^2\delta^2 g^2 t_d D_2), \qquad (10) \end{aligned}$$

where p_1 and p_2 are the fractions of molecules with the SDCs D_1 and D_2, respectively; $p_1 + p_2 = 1$. Equation 10 represents the two-phase model of adsorbate diffusion in a inhomogeneous porous system (Karger and Ruthven, 1992). The values of D_1 and D_2 were related to the diffusion processes in the regions significantly differing in their porosity. These data indicated a loss of connectivity between these regions with decreasing adsorbate content.

The different adsorption behavior of water and benzene on AC determined the different character of SDC of water and benzene during adsorption (Fig. 12).

As follows from Fig. 12, the average value of SDC of benzene in FAS-1, 3 reduces with decreasing pore filling (curves 1′, 3′). For $0.05 < \Theta < 0.2$, the value of D_{av} decreases by approximately a factor of three at $T = 303$ K. At the same temperature for FAS-1 the interval of the sharp decrease of SDC is shifted to larger benzene content.

The character of the dependence $D_{av}(\Theta)$ for water in AC differs from that for benzene. With decreasing pore filling at $0.2 > \Theta > 0$, the average value of water SDC in FAS-1, 2, 3 increases (curves 1, 2, 3, 4 on Fig. 12). Such dependences are characteristic of the effect of the "enhanced diffusion" displayed for self-diffusion of liquids in porous solids (D'Orazio et al., 1989; Dvoyashkin et al., 1991, Karger and Ruthven, 1992). This effect was explained by using the model of two phases, namely, liquid and gaseous (or vapor) occurring under the conditions of rapid exchange. As a result, the effective coefficient D_{av} is determined as

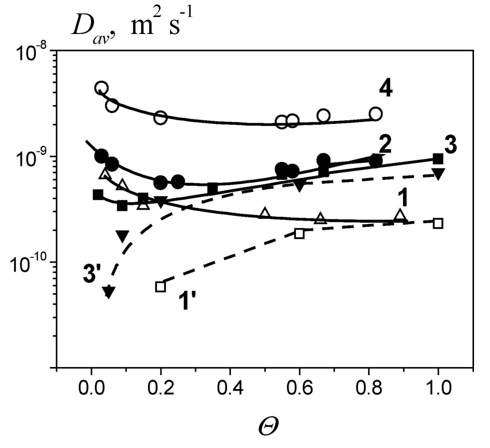


Figure 12. Dependences of the average value of self-diffusion coefficients of water (1, 2, 3, 4) and benzene (1′, 3′) on the filling of FAS-1 (1, 1′), FAS-2 (2) and FAS-3 (3, 3′) at $T = 303$ K and in FAS-2 (4) at $T = 333$ K.

follows:

$$D_{av} = N_l D_l + N_v D_v, \tag{12}$$

where N_l and N_v are the relative fraction of molecules in the liquid and vapor phases, respectively; D_l and D_v are the corresponding values of SDC. It was shown that the value of D_{av} is determined by the contribution of the molecules in the vapor phase, which, in turn, depends on the vapor pressure.

In mesopores of FAS-1, 2, 3 with a sufficiently large surface area 30–340 m^2/g (see Table 1) rapid exchange between the molecules in the adsorbed and vapor phases is quite probable. Consequently, the mean SDC of water in mesopores D_l, which is determined by Eq. (12), will decrease as Θ increases, thereby stipulating the dependence of the average SDC on filling in the range of Θ from 0 to 0.2. This conclusion was supported by the following experiment. In order to diminish the effect of the water molecules in the vapor phase (both in the mesopores and in the space between granules), we introduced liquid perfluorinated ester $C_{16}F_{34}O_4$ (invisible for our experiments) into the sample containing adsorbed water at $\Theta = 0.09$. Both of the diffusion decays are shown on Fig. 13.

The shape of DD observed in the modified sample occurred to be close to an exponential one (curve 2 on Fig. 13), while the value of the average SDC drastically decreases to $D_2 \sim 2{\cdot}10^{-10}$ m^2/s (Eq. (12)). Thus it may be assumed that the value D_2 in Eq. (12) characterises the mobility of water molecules in microporous zones of the AC under consideration. At the same time the dependence $D_{av}(\Theta)$ is determined by the contribution of diffusion in the vapor phase in mesopores within the range of $\Theta < 0.2$.

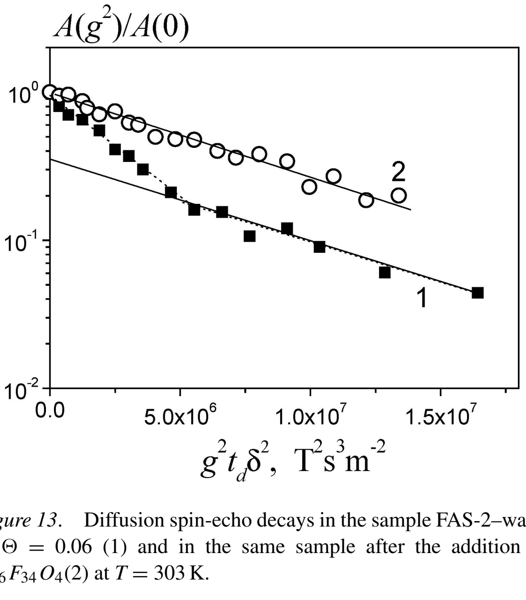


Figure 13. Diffusion spin-echo decays in the sample FAS-2–water at $\Theta = 0.06$ (1) and in the same sample after the addition of $C_{16}F_{34}O_4$(2) at $T = 303$ K.

When considering the SDC values of benzene as a function of the pore filling in FAS-1, 3 (curves 1′, 3′ on Fig. 12), the difference between the mechanism of adsorption of water and benzene has to be taken into account, which is revealed via different contributions of diffusion to the vapor phase in the mesopores of AC. Water is adsorbed primarily on PAS arranged both near the entry into the micropores and on the surface of the mesopores (Vartapetyan and Voloshchuk, 1995). This allows for the fast exchange with the vapor phase, in particular, in the mesopores. At the same time, the mechanism of micropore volume filling with benzene suggests that the filling of the narrowest micropores is more advantageous from the standpoint of energetics. So, the peculiarities of the observed dependences $D_{av}(\Theta)$ for benzene in AC are determined mainly by the increased tortuosity of the diffusion path in the micropores as well as by the increased interaction of the benzene molecules with the walls of the micropores in the course of the filling of the micropore volume.

Thus, the study of the translational mobility of water and benzene molecules in AC revealed a direct correlation between the specific features of the SDC of molecules in pores and the peculiarities of the mechanism of adsorption.

Comparison of the Self-Diffusion Behavior of Water in Adsorbents with Framework of Different Rigidity

It was found that the peculiarities of self-diffusion of adsorbed molecules are determined by the pore sizes and connectivity. From the other side, the introduction of the adsorbate also changes the adsorbent pore structure. In order to study the mutual influence between adsorbate and adsorbent, we compare the average diffusivities of water in microporous materials of different rigidity. Namely, the AC of FAS-type and polymer sorbents as Styrosorbs and the methacrylate polymer sorbents have been used.

The methacrylate polymer sorbents (MPS) have a similar structure and contain 40% of joining agent ethylendimethacrylate (EDMA) and 60% of monomers – 2,3-epoxypropylmathacrylate (EPMA). The original product sample (G-60) was modified by the hydrophilic amino groups of different base properties – diethylenetriamine (DETA), ammonia (AM) and mono ethanolamine (MEA), as well as hydrophobic benzyl groups (Bzl). The values of the primary adsorption centers, a_m, for adsorption of water vapor on these samples of MPS were determined as: 0.32, 1.30, 1.09, 0.96 and 0.10 mmol/g, respectively. The maximum water adsorption values were: 14.2, 27.9, 21.3, 45.9, and 1.6 mmol/g, respectively for G-60, DETA, AM, MEA, and Bzl samples.

It was found that the manner of the introduction of water into MPS determined the behavior of the system water–MPS. In contrast to the systems AC–water and Styrosorb–water, for water adsorbed on MPS from the vapor phase a stimulated echo was not observed up to the maximum value of adsorption. Most likely the molecules of adsorbed water filled the smallest pores and were characterized by short values of T_2 and, consequently, were invisible in the stimulated spin-echo experiments. The other MPS samples were saturated by water with the subsequent evaporation of water. The extend of water filling of the MPS pores, Θ, was considered as a ratio of the mass of adsorbed water to the mass of the MPS sample (in some cases Θ exceeds 1). The same procedure of pore filling by water was used for Styrosorbs and AC. It should be noted that the features of AC samples (FAS-4, 5, 6) are close to those of FAS-1, 2, 3 differing only in the PAS amounts. The values of a_m, determined from the comparison plots for FAS-4, 5, 6, are equal 0.20, 0.08, 0.05 and 0.09 mmol/g, respectively.

Figures 14(a), (b) and (c) show the SDC of water in AC (FAS-4, 5, 6), Styrosorbs and MPS samples, respectively, as a function of the pore filling Θ, measured at 303 K.

The open symbols denote the data for the samples filled by water from the vapor phase, the arrows on Figs 14(a) and (b) show the data of the samples with maximum filling from the vapor phase.

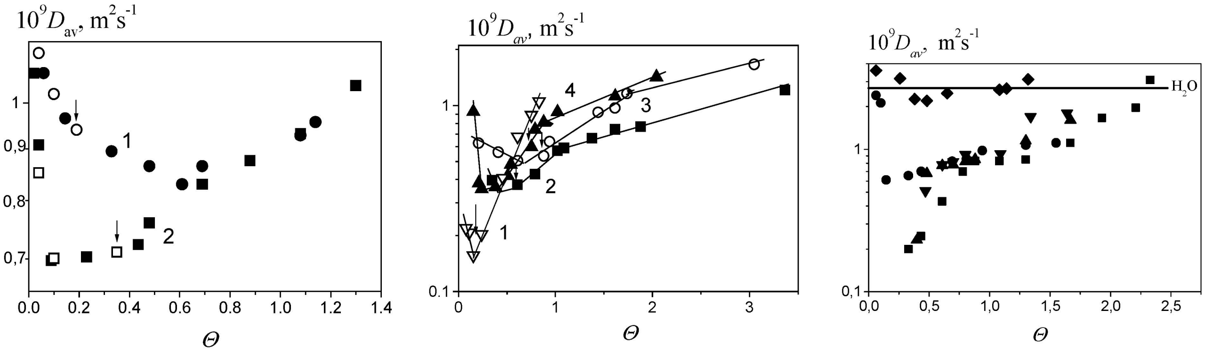
It is obvious that the diffusivities were not affected whether water was introduced into the AC and Styrosorbs pores from the vapor or the liquid phase.

The features of the dependences of $D_{av}(\Theta)$ observed in AC and Styrosorbs are similar, so the diffusional behavior of water in the AC with the relatively rigid framework may be assumed to be similar to that in the super-crosslinked Styrosorbs, MN-100 and MT-65. The effect of enhanced diffusion is observed for low pore filling (see Fig. 14(a) and (b)) and is the result of fast exchange between the liquid and vapor phase in the meso- and macropores of AC and Styrosorbs.

The increase of the SDC values with water content for large Θ is due the buildup of water in the large pores and the enlarged connectivity of the pore space.

It has been found that the minimum position on the dependence $D_{av}(\Theta)$ is shifted to the interval of larger filling extent (curves on Fig. 14(b)). No influence of the PAS amount on the character of the $D_{av}(\Theta)$ curves was noticed for AC as well as for Styrosorbs (see Table 1, 2 and Figs 14(a) and (b)).

The SDC of water in MPS filled from the liquid phase exceed that measured in AC and Styrosorbs and are close to the bulk value. Unlike AC and Styrosorbs, the PAS amount in MPS affect the diffusivity of adsorbed water (Fig. 14(c)). Indeed, the largest SDC values of



(a) (b) (c)

Figure 14. a, b, c Average value of SDC of water as a function of pore filling (a) – in PS: MN-100 (•) and MT-65 (■); (b)—in AC: FAS-4 (•), FAS-5(■), FAS-6(▲), FAS-7(▼); (c)—in MPS: G-60(•), G-60-DETA(■), AM(▲), MEA(▼) and Bzl(♦). The open symbols indicate the data for samples filled from the vapor phase. The arrows mark samples with a limited filling from the vapor phase.

water for all fillings were observed for the modified hydrophobic MPS - Bzl (curve 5 on Fig. 14c), while the smallest diffusivity characterizes water in the pores of hydrophilic MPS (DETA). Thus, the distribution of PAS in MPS determines the distribution of the water molecules in the pores of different sizes, which, as a consequence, influence the mobility of the adsorbed molecules.

As the most outstanding distinction of MPS, however, the manner of filling of pores by water was found to be a determining factor for the behavior of adsorption systems. Thus, for MPS samples filled by water from the liquid phase with subsequent evaporation, the diffusion measurements have been performed in all intervals of water content. At the same time a spin-echo was not observable for MPS filled from the water vapor phase. As a most probable explanation, the changes of the MPS porous structure due to the swelling of MPS for water adsorption from liquid phase are considered.

Hence, the obtained results of diffusion measurements indicate that in the case of water adsorption the Styrosorbs, namely MN-100 and MT-65, are adsorbents with a relatively rigid framework, similar to active carbons of type FAS. Nuclear magnetic relaxation studies of adsorbed water and benzene in PS showed that, the influence of water on Styrosorb porous structure on swelling of MN-100 or MT-65 was not so essential as with benzene. At the same time, the self-diffusion measurements revealed that an introduction of water from the liquid phase into the methacrylate polymer sorbents induces changes of MPS due to swelling.

Conclusion

The important information on the porous structure of the adsorbents (AC and polymer sorbents) could be obtained by an analysis of the relaxation times of benzene and water in the pores of the adsorbents under study. The obtained estimates agree with established adsorption mechanisms of benzene and water on AC.

The analysis of the diffusion decays of the stimulated echoes in the self-diffusion measurements in the adsorption systems AC-water and AC-benzene enables us to evaluate the dimensions of zones of different porosities.

The nuclear magnetic relaxation study of water and benzene in super-crosslinked polymer sorbents, Styrosorbs, detected a predominant deposition of benzene molecules in the larger pores compared with water in Styrosorbs and benzene in AC.

The self-diffusion measurements of water molecules introduced into methacrylate polymer sorbents from the liquid phase indicate a possible swelling of MPS in water. The mobility of the water molecules adsorbed in the modified hydrophobic and hydrophilic MPS differs.

The obtained data of nuclear magnetic relaxation and self-diffusion of the adsorbed water and benzene in the sorbents with framework of different rigidity, active carbons and polymer sorbents, are in accordance with the adsorption investigations and complement them.

Nomenclature

$A(g^2)$	normalized spin-echo amplitude on the square of the pulse field gradient in the PFG NMR experiments
a	absolute adsorption (mmol/g)
a_m	number of PAS (mmol/g)
a_s	limitary value of adsorption (mmol/g)
D	self-diffusion coefficient (m^2/s)
D_{av}	average value of self-diffusion coefficient (m^2/s)
D_l	self-diffusion coefficient of molecules in liquid phase (m^2/s)
D_v	self-diffusion coefficient of molecules in vapor phase (m^2/s)
N_l	relative fraction of molecules in liquid phase
N_v	relative fraction of molecules in vapor phase
$G(t)$	normalized signal of free induction decay
g	magnetic field gradient (T/m)
l	dimension of the areas of porous material filled by adsorbate characterized by a single SDC of adsorbate (μm)
$M(t)$	normalized nuclear magnetization decay
p/p_s	relative pressures
$P(T_2)$	distribution of spin-spin relaxation times
$P(x_i)$	distribution of pore sizes
$p(D)$	distribution of self-diffusion coefficients
S	specific pore surface (m^2/g)
S_g	geometric micropore surface area ((m^2/g)
S_{BET}	specific surface of pores determined from BET equation (m^2/g)
S_{me}	surface area of mesopores (m^2/g)
t	time (s)
t_d	separation of the field gradient pulses, “diffusion time” (s)
T_1	spin-lattice relaxation time (s)
T_2	spin-spin relaxation time (s)

T_{2av}	average value of spin-spin relaxation time (s)
$\mathbf{L}$	width of micropores (nm)
V	pore volume (m^3)
V_g	maximum pore volume ($cm^3 \cdot g^{-1}$)
W_2	second momentum of NMR absorption line
W_0	micropore volume (cm^3/g)
w	relative mass content of adsorbed molecules
x	pore size (nm)
γ	gyromagnetic ratio (Hz/T)
δ	dispersion of micropore volume distribution (nm)
δ	duration of pulsed magnetic field gradient (μs)
λ	thickness of surface layer (nm)
μ	density of surface sinks of magnetization ($m\ s^{-1}$)
Θ	degree of pore filling by adsorbed molecules
σ	parameter of width of $p(D)$
τ	time interval between RF pulses (ms)

References

Ainscough A.N. and D. Dollimore, "Adsorption Capacity of Molecular Sieve Type Carbons," *Langmuir*, **3**, 708–713 (1987).

Babaev P.I., M.M. Dubinin, and A.A. Isirikyan, "Specific Features of Sorption Energetics on Microporous Adsorbents," Dokladi AN SSSR, 233, 1122–1124 (1977). (In Russian).

Belyakova, L.D., V.A. Davankov, M.P. Tsyrupa, and T.I. Shevchenko, "Sorption of Vapors of Various Substances by Hypercrosslinked "Styrosorbs" Polystyrenes," *Adv. Collid and Int. Sci.*, **25**, 249–266 (1996).

Brownstein, K.R. and C.E. Tarr, "Spin-Lattice Relaxation in a System Governed by Diffusion," *J. Magn. Reson.*, **26**, 17–24 (1977).

Brownstein, K.R. and C.F. Tarr, "Importance of Classical Diffusion in NMR Studies of Water in Biological Cells," *Phys. Rev. A.*, **19**, 2446–2453 (1979).

Carr, H.Y. and E.M. Purcell, "Effects of Diffusion on Free Precession in Nuclear Magnetic Resonance Experiments," *Phys. Rev.*, **94**, 630–638 (1954).

Davankov, V.A. and M.P. Tsyrupa, "Structure and Properties of Hypercrosslinked Polystyrene-the First Representative of a New Class of Polymer Networks," *Reactive Polymers*, **13**, 27–42 (1990).

D'Orazio, F., J.C. Tarcson, W. Halperin, K. Eguchi, and T. Mizusaki, "Application of Nuclear Magnetic Resonance Pore Structure Analysis to Porous Silica Glasses," *J. Appl. Phys.*, **65**, 742–751 (1989).

D'Orazio, F., S. Bhattacharia, W.P. Halperin, and R. Gerhardt, "Enhanced Self-Diffusion of Water in Restricted Geometry," *Phys. Rev. Letter*, **63**, 42–46 (1989).

Dubinin, M.M., "Microporous Structures of Carbonaceous Adsorbents," *Carbon*, **20**, 3, 195–200 (1982).

Dubinin, M.M., "Microporous Structures and Adsorption Properties of Carbonaceous Adsorbents," *Carbon*, **21**(4), 359–366 (1983).

Dubinin, M.M., A.A. Isirikyan, and N.I. Regent, "Heats of Water Adsorption on Oxidized Active Carbon," *Izvestia AN SSSR, Ser. Khim.* 233–237 (1987) (In Russian).

Dubinin, M.M., R.Sh. Vartapetyan, A.M. Voloshchuk, J. Karger, and H. Pfeifer, "NMR Study of Translational Mobility of Molecules Adsorbed on Active Carbons," *Carbon*, **26**, 515–520 (1988).

Dvoyashkin, N.K., V.D. Skirda, A.I. Maklakov, M.V. Belousova, and R.R. Valiullin, "Peculiarities of Self–Diffusion of Alkane Molecules in Kaolinite," *Appl. Magn. Res.*, **2**, 83–88 (1991).

Fenelonov, V.B. *Porous carbon*, Nauka, Novosibirsk, 1995. (In Russian).

Godefroy, S., J.-P. Korb, M. Fleury, and R.G. Bryant, "Surface Nuclear Relaxation and Dynamics of Water and Oil in Macroporous Media", *Phys. Rev. E.*, **64**, 21605–21618 (2001).

Gregg, S.J. and K.S.W. Sing, *Adsorption, Surface Area and Porosity.* Second Ed. Academic press, New York, 1982.

Hills, B.P. and J.E. Snaar, "Water Proton Relaxation Studies of Pore Microstructure in Monodisperse Glass Bead Beds," *Molecular Physics*, **84**, 141–157 (1995).

Idiyatullin, D.Sh., V.D. Skirda, and V.S. Smirnov, USSR Patent 1578608. *Bull. Patents*, 9854 (1990).

Karger, J., "Zur Bestimmung der Diffusion in einem Zweibereichsystem mit Hilfer von gepulsten Feldgradienten," *Ann. Phys.*, **24**, 1–4 (1969).

Karger, J., Ruthven, D.M., *Diffusion in Zeolites and Other Microporous Solids*, John Wiley and sons, New York, 1992.

Karger, J., H. Pfeifer, R.Sh. Vartapetyan, and A.M. Voloshchuk, "Molecular Self-Diffusion in Active Carbons," *Pure Appl. Chem.*, **61**, 1875–1880 (1989).

Karnaukhov, A.P., *Adsorption. Texture of Disperse and Porous Materials*, Nauka, Novosibirsk. 1999 (In Russian).

Kleinberg, R.L., W.E. Kenyon, and P.P. Mitra, "Mechanism of NMR Relaxation of Fluids in Rocks," *J. Magn. Reson. Ser. A*, **108**, 206–214 (1994).

Khozina E.V., R.Sh. Vartapetian, and D.Sh. Idiyatullin, "Features of Nuclear Magnetic Relaxation of Water and Benzene Molecules During Absorption on Activated Carbons and Estimation of Pore Size Distribution in Adsorbents," *Russ. Chem. Bull.*, **51**, 2036–2043, (2002).

Levitt, M.H., R. Freeman, "Compensation for Pulse Imperfections in NMR Spin Echo Experiments," *J. Magn. Reson.*, **43**, 65–72 (1981).

Maklakov, A.I., V.D. Skirda, and N.F. Fatkullin, "Self-Diffusion in Polymer Systems". In: *Encyclopedia of Fluid Mechanics*, 9, N.P. Cheremisinoff, (Ed.), Gulf-Publishing CO, Houston, Chapter 2, p. 705, 1990.

Meiboom, S. and D. Gill, "Modified Spin-Echo Method for Measurement of Nuclear Relaxation Times," *Rev. Sci. Instr.*, **29**, 6881–6885 (1958).

Michail, R.Sh., S. Brunauer, and E.E. Bodor, "Investigations of a Complete Pore Structure Analysis. I. Analysis of micropores," *J. Colloid. Int. Sci.*, **26**, 45–53 (1968).

Pfeifer, H., "Surface Phenomena Investigated by NMR," *Phys. Report.*, **26**, 294–338 (1976).

Platonova, N.P., O.G. Tataurova, R.S. Vartapetjan, A.M. Voloshchuk, and J. Hradil, "Adsorption of Water Vapour on Modified

Methacrylate Polymeric Sorbents," *Russ. Chem. Bull.*, **44**(11), 2068–2072 (1995).

Stallmach, F. and J. Karger, "The Potentials of Pulsed Field Gradient NMR for Investigation of Porous Media," *Adsorption*, **5**, 117–133 (1999).

Stejescal, E.O. and J.E. Tanner, "Spin-Diffusion Measurements: Spin-Echoes in the Presence of a Time-Dependent Field Gradient," *J. Chem. Phys.*, 42, 288–292 (1965) Stoeckli, H.F., P. Rebstein, L. Ballerini, "On the Assessment of Microporosity in Active Carbons, a Comparison of Theoretical and Experimental Data," *Carbon*, **28**, 907–909 (1990).

Vartapetyan, R.Sh., A.M. Voloshchuk, M.M. Dubinin, J. Karger, and H. Pfeifer, "Adsorption and Mobility of Water and Organic Substances in the Carbon Adsorbents. I. Investigations of Water Molecules Mobility in Active Carbons with Various Micropore Structures using PFG MNR Method," *Bull. Acad. Sci. USSR, Div. Chem. Sci.*, **34**, 2241 (1985).

Vartapetyan, R.Sh., A.M. Voloshchuk, M.M. Dubinin, J. Karger, H. Pfeifer, and H.W. Heink, "Adsorption and Mobility of Water and Organic Substances in the Carbon Adsorbents. IV. Self-diffusion Coefficients of Water and Organic Substances in Active Carbon with Relatively Wide Micropores," *Izvestia AN SSSR. Ser. Khim.*, 1949–1951 (1989) (In Russian).

Vartapetyan, R.Sh. and A.M. Voloshchuk, "The Mechanism of Adsorption of Water Molecules on Carbon Adsorbents," *Russian Chem. Rev.*, **64**, 985–1001 (1995).

Vartapetyan, R.Sh., A.M. Voloshchuk, A.A. Isirikyan, N.S. Polyakov, and Y.I. Tarasevich, "Chemistry of Carbon Surface and Mechanism of Water Molecule Adsorption," *Colloid and surfaces A*, **101**, 227–232 (1995).

Vartapetyan, R.Sh., A.M. Voloshchuk, M.M. Dubinin, and T.S. Yakubov, "Adsorption of Wwater Vapour and Microporous Structures of Carbon Adsorbents. 14. Differential heats of adsorbtion of water vapour on active carbons," *Izvestia AN SSSR. Ser. Khim.* 1934–1938 (1987) (In Russian).

Vartapetyan, R.Sh., A.M. Voloshchuk, M.M. Dubinin, L.A. Chekulina, and S.G. Chepurnoy, "Adsorption of Water Vapour and Microporous Structures of Carbon Adsorbents. 11. Features of adsorption of water vapour on ultramicroporous active carbons," *Izvestia AN SSSR, Ser. Khim.*, 2407–2412 (1986) (In Russian).