Sorption of nitrogen-containing aromatic compounds on ultradispersed diamonds

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Adsorption of a number of aniline and pyridine derivatives from water-acetonitrile solution on ultradispersed diamonds was investigated using dynamic sorption method. It was shown that the nature of functional substitutes and their position in molecules of nitrogen-containing compounds of pyridine and aniline have a pronounced effect on adsorption on the surface of ultradispersed diamonds. The dependence of chromatographic sorbate retention on the content of mobile phase could be described by a curve with a minimum. Such nonlinear relationship was explained by the change in the ratio of contribution of specific and non-specific interaction to the sorbate retention that was observed on varying the volume content of an organic component in mobile phase. The influence of temperature on sorption of pyridine and aniline derivatives on ultradisperesed diamonds was investigated. The changes in enthalpy and entropy factors of competitive sorption of sorbates were determined.

Key words: ultradispersed diamonds, sorbtion, concentrating, aniline derivatives, pyridine derivatives, high performance liquid chromatography.

A number of requirements is imposed on the sorbents used in high performance liquid chromatography (HPLC). Their mechanical strength must be high enough for operations under high pressure, while reasonable thermal stability is also needed. Moreover, volume changes of a sorbent in organic solvents or water solutions should not occur if pH or ionic strength of the medium is varied. Sorbents should not contain reactive groups that favour irreversible sorbate adsorption. Finally, sorbents are expected to be selective in adsorption/separation of the samples analyzed. For many years materials based on silica gels or organic polymers were the main types of adsorbents applied in HPLC. Silica gel sorbents are characterized by mechanical strength[1] and their surface can be modified easily to increase or change the selectivity of chromatographic separation. But these sorbents have low hydrolytic stability, as they have propensity to hydrolysis in a strong acid or basic media, and relatively low thermal stability in water and water-organic eluents. Moreover, silica gel sorbents have residual silanole surface groups, responsible for irreversible adsorption of the commonly used adsorbates.[2,3] Organic polymer sorbents besides their high hydrolytic stability do not comply with all the demands imposed for the sorbents for HPLC due to swelling in organic solvents and relatively low mechanical strength of particles. So the search and development of new sorbents based on hydrolytically stable supports that meet all the requirements for HPLC sorbents is an important and topical problem.

There is a great interest to the works on the synthesis and investigation of adsorption and other properties of carbon nanomaterials such as ultradispersed diamonds (UDD). They are characterized by mechanical and thermal stability, as well as resistance to hydrolysis in a wide range of pH. They show no shrinkage or swelling in organic liquids. Besides, with the development of new technologies of synthesis[4] diamonds became cheaper and more available for applications as adsorbents.[5,6] As in any nonporous material a high specific surface area of diamond can be developed only due to an increase in dispersion. Recently, detonation-synthesized nanodiamonds (UDD, nanodiamonds), with specific surface area up to 300—400 $m^2 g^{-1}$, became widely available.[7]

According to literature data[8,9] diamond nanoparticles consist of diamond nucleus, external carbon shell and a layer of functional groups (hydroxyl, carboxyl etc.).[10] The IR-spectroscopy method serves to detect different functional groups on nanodiamond surface:[7,11,12] oxygen-containing (hydroxyl, carbonyl, ether, anhydride ets) nitrogen-containing (amine, amide *ets.*) and others. Almost any IR spectrum shows carbonyl (1730—1790 cm^{-1}) and

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hydroxyl (1640, 3400 cm^{-1}) functional groups.[13–17] Thus, UDD could be considered as a low-polarity adsorbent, capable of both specific and non-specific interactions.

In liquid chromatography, when polar adsorbents and polar eluents (water-organic) are applied as a sorption system the so-called hydrophilic chromatography mode is applied.[18] In this case water-organic eluents with a high content of organic modifier (more than 70% v/v), usually as methanol or acetonitrile, are used to develop strong hydrophilic interactions between sorbates and the sorbent surface.[19] The main advantage of the hydrophilic chromatography is a highly selective separation of polar compounds, which are slightly soluble in non-polar eluents. The mechanism of retention in some cases is not clear. Probably it includes some features typical of reverse-phase liquid chromatography (RP-HPLC), normal-phase liquid chromatography (NP-HPLC) or ion-exchange chromatography (IEC).[20–22] The «mixed mode» of adsorption is supposed to occur in hydrophilic chromatography. When this mechanism is operative, specific and non-specific interactions compete and the polarity of an eluent defines the adsorption behavior of an adsorbent (performance of reverse-phase or normal-phase liquid chromatography type).[23]

Posibilities of UDD application in gas[24] and liquid[25–27] cromatography are discussed by many authors. There are some works on the modification of nanodiamond surface,[28] including the introduction of metal nanoparticles followed by examination of sorption properties of the surfaces modified.[29] Application of UDD in the solid phase extraction (SPE), a widely used method of sample preparation, is also described.[30] One of the most important and practically significant problem is SPE of vitamins. [31,32] Vitamins are complicated organic compounds that can include, for example, heterocyclic substitutes (pyridine derivatives) or fragments of amino-containing aromatic systems (aniline derivative) in their structure. The mechanism of retention of complicated vitamin molecules on different adsorbents is not properly understood. However, the results obtained in the studies of physicochemical characteristics of sorption of aniline and pyridine derivatieves can be interpretated taking into account the behavior of vitamin molecules in a sorption system.

Physicochemical properties of nanodiamonds and especially their sorption capacity are still not sufficiently studied. However, the knowledge of these properties is important to study the kinetics of sorption, to investigate the mechanism of sorbate-sorbent interaction and to develop the theory of methods of separation and concentrations on UDD.

The goal of the present work is to study adsorption properties of UDD using the method of dynamic sorption, to detect the effect of the sorbate nature on its retention on UDD and to investigate the effect of the mobile phase composition (MP) and the column temperature on adsorption of model sorbates.

Experimental

Chromatographic system. A liquid cromatograph Shimadzu LC-20 Prominence (Shimadzu, Japan), equipped with two high-pressure pumps (LC-10Ai) and UV—Vis detector Shimadzu SPD-10Avp (λ =190—370 nm) was used. The fraction of UDD («ALIT», Kiev, Ukraine) containing microparticles of diameter of 3.5—4.5 μm with specific surface of 191 $m^2 g^{-1}$ and effective average pore diameter of 4 nm was used for packing of stainless steel chromatographic column 50×4.6 mm ID. The column hold-up volume V_M was 0.2 mL. Van Deemter curve was plotted (Fig. 1) and the optimal conditions of the chromatographic experiment, allowing operations under conditions close to equilibrium were selected. The optimal eluent flow rate was 0.5 mL min^{-1}. The influence of temperature on retention of a sorbate was studied in the range from 45 to 65 °C. The column was conditioned at least for one hour after any changes in composition of MP. Different water-acetonitrile solutions were used as mobile phase: MeCN : H_2O = 70 : 30, 60 : 40; 50 : 50, 40 : 60, 30 : 70.

Based on experimental data chromatographic and thermodynamic characteristics of sorbtion of the studied substances were determined.

The values of retention factor were calculated according to the Eq. (1):[33]

$$k = (t_R - t_M)/t_M, \quad (1)$$

where t_R is the total retention time of the studied substance, min; t_M is the hold-up time (retention time of non-sorbed compound (benzoic acid)), min.

Number of theoretical plates (N) and a height equivalent to a theoretical plate (H) of the given chromatographic column were determined using Eqs (2) and (3):[34]

$$N = 5.454(t_R/\tau_h)^2, \quad (2)$$

$$H = L/N, \quad (3)$$

where t_R is total retention time of a sorbate, min; τ_h is the peak width at half-height expressed in time unit, min; L is the column length, mm.

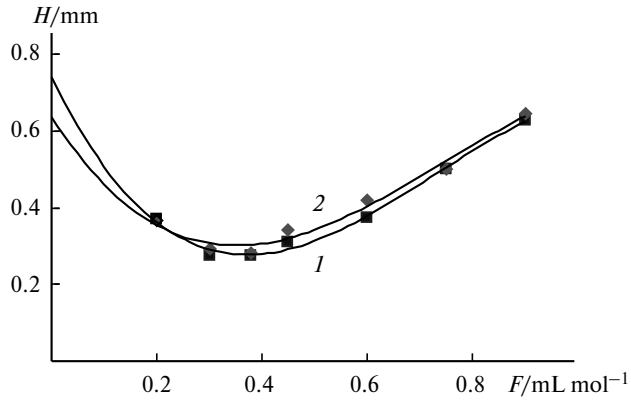


Fig. 1. Dependence of height equivalent to a theoretical plate (H) on eluent flow (F) for the column with ultradispersed diamonds (50×4.6 mm). Eluent is MeCN—H_2O (40 : 60), sorbates: pyridine (*1*), aniline (*2*).

Adsorption equilibrium in chromatographic system is described by the known equation of chemical thermodynamics (4):[33]

$$\Delta G = \Delta H - T\Delta S, \quad (4)$$

where ΔG, ΔH and ΔS are the changes in Gibbs free energy, enthalpy and entropy respectively.

The dependence between the isobaric potential ΔG and the partition coefficient K_c (5), which is the distribution ratio of a sorbate between the mobile and stationary phases, is defined.[35]

$$\Delta G = -RT\ln K_c. \quad (5)$$

The retention factor is related to the partition coefficient by Eq. (6):[35]

$$K_c = k/\varphi. \quad (6)$$

Thus, the dependence of the retention factor versus temperature can be expressed by Eq. (7):[33]

$$\ln k = -\Delta H/(RT) + \Delta S/R + \ln\varphi, \quad (7)$$

where k is the retention factor, φ is the phase ratio for a chromatographic column, R is gas constant.

The phase ratio in the chromatographic column was determined from Eq. (8):[35]

$$\varphi = V_S/V_M, \quad (8)$$

where V_S and V_M are volumes of stationary and mobile phases correspondingly, which were calculated from the hold-up volume of the column V_M and the inner volume of the column (50×46 mm).

The primary chromatographic data were approximated within an error of 2—3%.

Reagents and solvents. HPLC grade acetonitrile, (Panreac, Spain), ethanol 96% (Reakhim, Moscow, Russia), deionized water obtained using system Portlab D-301 (Moscow, Russia) were used. The standart solutions of the following substences (Sigma, USA) were used: pyridine (**1**), quinoline (**2**), indole (**3**), *N*,*N*-dimethyl-4-aminopyridin (**4**), 2-methylpyridine (**5**), 2-ethylpyridine (**6**), 2,6-dimethylpyridine (**7**), aniline (**8**), 4-methylaniline (**9**), 1,4-diaminobenzene (**10**), acetanilide (**11**), *N*,*N*-dimethylaniline (**12**), and *N*,*N*,*N*′,*N*′-tetramethyl-*p*-phenylenediamine (**13**). Some physicochemical characteristics of these compounds are listed in Table 1.[36—39]

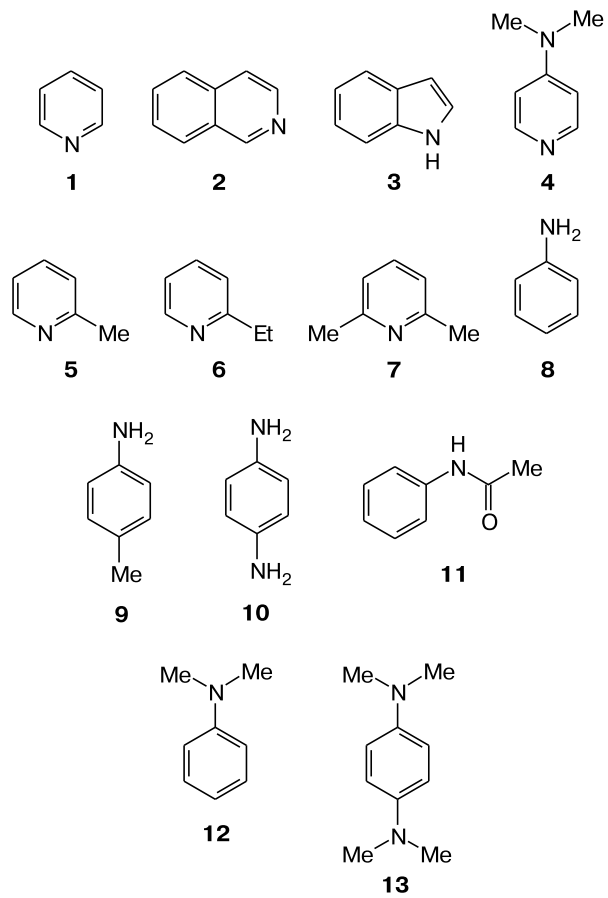


Table 1. Physicochemical characteristics of selected sorbates

Sorbate	M_r[36]	pK_{BH^+}[38,39]	$\log P$[36]	μ[37]	α[36,38]	V[36]	MR[36]
1	79.11	5.23	0.65	2.20	9.73	82.7	23.84
2	129.16	4.94	2.06	2.25	17.00	116.8	40.29
3	117.15	−2.40	2.14	2.11	14.49	101.9	38.20
4	122.17	—	1.34	3.17	15.30	120.6	38.70
5	93.13	5.97	1.10	1.72	11.56	98.9	33.17
6	107.16	5.90	1.72	1.67	13.40	115.5	33.90
7	107.16	6.60	1.65	1.52	13.50	115.2	34.00
8	93.13	4.58	0.94	1.48	11.79	91.7	30.76
9	107.15	5.12	1.39	1.27	13.62	108.0	35.80
10	108.14	6.08	0.48	0.02	13.14	94.0	35.46
11	135.17	0.40	−0.29	2.87	15.54	133.7	43.95
12	121.18	5.15	2.31	1.58	15.46	127.4	40.49
13	164.25	6.35	2.08	0.05	20.48	165.4	54.92

Note. M_r *is* molecular weight, g mol^{-1}; pK_{BH^+} is acid capacity value; $\log P$ is logarithm of distribution ratio in the system *n*-octanol—water; μ is dipole moment of the molecule, D; α is molecule polarizability, Å^3; V is molecular volume, Å^3; MR is molecular refractivity, mol cm^{-3}.

Results and Discussion

The influence of the mobile phase composition on the adsorption of the nitrogen-containing aromatic compounds on UDD. The dependences of the logarithm of retention factor (lnk) on the volume content of acetonitrile in mobile phase are shown in Fig. 2. The obtained curves have a non-linear shape with a minimum occurring at the content of acetonitrile in MP of 50-60 vol.%. With an increase in the acetonitrile concentration from 20 to 50 vol.% the retention gradually decreases, while it increases with higher acetonitrile content. This correlation can be explained by changes in contribution of specific and non-specific interaction to the sorbate retention which became apparent when the volume content of acetonitrile in MP is varied.[40,41]

Non-linear relationships between sorbate molecule adsorption and mobile phase composition on the UDD surface (see Fig. 2) can be interpreted from the viewpoint of competitive nature of sorption from solutions. At a small acetonitrile content in MP highly polar water molecules are adsorbed on hydrophilic adsorption sites of the UDD surface (hydroxy- and carboxyl-groups) and the competition between sorbate molecules and water molecules of mobile phase increases.[43] As a result the sorbate molecules are retained on the adsorbent surface mainly due to non-specific intermolecular interactions. With an increase in the acetonitrile content in MP up to 60 vol.% the concentration of the molecules of organic modifier at the surface of stationary phase increases and competition between adsorbed molecules and acetonitrile molecules for the hydrophobic sites of the adsorbent surface becomes stronger.[44] This leads to the increasing role of specific interactions in rention of sorbate molecules on the adsorbent surface.

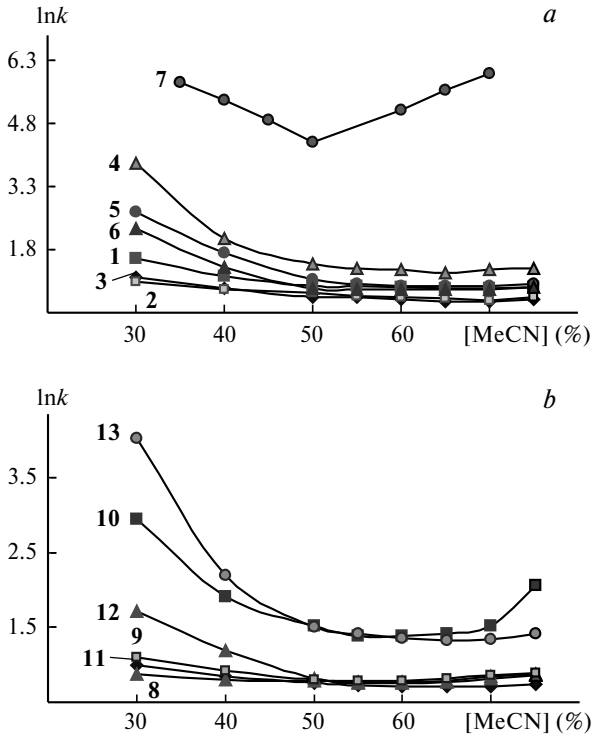
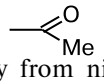


Fig. 2. Dependence of logarithm of retention factor for pyridine **1**—**7** (*a*) and aniline **8**—**13** (*b*) derivatives on volume concentration of organic modifier in MP.

In the case of sorption of aromatic compounds with different functional substitutes the retention order is governed by the electron density in benzene ring. The latter depends on the type of substitutes (electron-donor or electron-acceptor), changes in polarizability and orientation of molecules in relation to the adsorbent surface, shielding of polar functional groups by non-polar groups and possible formation of an intramolecular hydrogen bonds between adjacent polar functional substitutes.[45]

When the MP with a high content of acetonitrile (70—80 vol.%) is used sorbate retention mainly depends on specific intermolecular interactions between sorbate molecules and the adsorbent surface. At the ratio MeCN : H_2O = 70 : 30 the order of increasing total retention for nitrogen-containing heterocyclic compounds is: indole (retention factor k = 1.75, pK_{BH^+} = –2.4) < quinoline (k = 1.82, pK_{BH^+} = 4.94) < pyridine (k = 2.40, pK_{BH^+} = 5.23) (see Table 1 and Fig. 2, *a*), reflecting the increase in basicity of the compound. That gives evidence of acidic nature of UDD surface (domination of hydroxy- and carboxyl-groups on the adsorbent surface).

Introduction of electron-donor methyl group in the second position in the pyridine molecule results in the increasing electron density on the nitrogen atom, i.e. increase in basicity of the compound (pK_{BH^+} for pyridine and 2-methylpyridine constitute 5.23 and 5.97 respectively) and its retention (retention factor for 2-methylpyridine is k = 2.54). Similarly, introduction of the second methyl group into the 6th position leads to enhanced adsorption (k = 3.75, pK_{BH^+} = 6.60) at the acetonitrile concentration in MP of 70 vol.%. The methyl groups do not give rise to steric hindrance when 2,6-dimethylpyridine is adsorbed. However the presence of an ethyl group in the 2nd position in pyridine molecule provokes a decrease in the retention (k = 2.34) because adsorption gives rise to steric hindrance. Shielding of the nitrogen atom in pyridine ring may be the reason for a decrease in the adsorption of 2-ethylpyridine on UDD.

At MeCN : H_2O = 70 : 30 in a series of aniline derivatives (see Fig. 2, *b*) the retention increases in the row: acetanilide (retention factor k = 2.04) < *N*,*N*-dimethylaniline (k = 2.26) < aniline (k = 2.32) < 4-methylaniline (k = 2.35) < *N*,*N*,*N*′,*N*′-tetramethyl-p-phenylenediamine (k = 3.82) < 1,4-diaminobenzene (k = 4.59). The presence of electon-accepting  group in acetanilide shifts the electron density from nitrogen atom to the acetate group and increases acidity of the substance

(pK_{BH^+} = 0.4).[46] Substitution of hydrogen atoms by methyl groups in amino group of aniline leads to a steric hindrance during sorption and *N*,*N*-dimethylaniline retained more weakly than aniline. Introduction of electron-donating methyl group to *para*-position in aniline molecule explains the increase in the basicity of 4-methylaniline (pK_{BH^+} for aniline and 4-methylaniline is 4.58 and 5.12 respectively) and its retention. The presence of two amino groups in 4-diaminobenzene leads to a greater increase in basicity (pK_{BH^+} = 6.08) and retention. If four hydrogen atoms of amino groups of 1,4-diaminobenzene are substituted, as in the case of *N*,*N*-dimethylaniline, the steric hindrance arises during adsorption and *N*,*N*,*N*′,*N*′-tetramethyl-*p*-phenylenediamine (k = 3.82, pK_{BH^+} = 6.35) is retained weaker than non-substituted 1,4-diaminobenzene (k = 4.59, pK_{BH^+} = 6.08).

Thus, one of the factors which governs the retention of a number of aniline and pyridine derivatives on UDD is basicity of the compound. However, at MeCN : H_2O = = 70 : 30 the correlation coefficient R^2 for dependencies between retention of aniline and pyridine derivatives and values of acidity of the base was 0.442 and 0.428 correspondingly. This gives evidence that the value of acidity of the base is not the main parameter that determines the retention of selected sorbates. Nevertheless the correlation coefficient becomes worse if the former parameter is excluded from the regression analysis of the data. Apart from the value of the base acidity, the other parameters such as molecular volume, dipole moment, logarithm of distribution factor in the 1-octanol—water system, polarizability, molecular refraction (see Table 1) can be used to describe the influence of chemical structure on their adsorption (chromatographic retention). For the measured retention values, at MeCN : H_2O = 70 : 30 and the column temperature of 45 °C, the correlations with some molecular descriptives were calculated and analyzed. The correlation coefficients are presented in Table 2.

The data in Table 2 show that the best correlations are achieved when retention is compared with dipole moment, polarizability and acidity of the base molecule. Moreover, the retention increases with a decrease in the dipole moment and increase in the acidity of the base.

For MPs with a small content of acetonitrile (10—20 vol.%) the retention of sorbates is determined mainly by non-specific intermolecular interactions. At MeCN : H_2O = 30 : 70 the order of increasing retention for nitrogen-containing heterocyclic compounds (see Fig. 2, *a*) is: quinoline (retention factor k = 2.82) < indole (k = 3.13) < pyridine (k = 4.84). Increase in the retention of condensed aromatic structures such as indole and quinoloine, compared to pyridine can be explained by the increasing volume of molecules (101.9, 116.8 and 82.7 Å^3 for indole, quinoline and pyridine respectively). It appeares that primary sorbate and water molecules compete for the adsorbent surface. When water content in MP is high enough water molecule shield active polar sites of the sorbent surface and their displacement by bigger molecules of quinilone and indole requires more energy.

Introduction of electron-donor methyl group into the second position in the pyridine molecule increases electron density in a benzene ring and, as consequence, the retention of 2-methylpyridine (retention factor k = 14.74 and 4.84 for 2-methylpyridine and pyridine respectively). Similarly, introduction of the second methyl group to the 6th position results in a stronger adsorption of 2,6-dimethylpyridine (k = 46.69) compared to pyridine. The presence of ethyl group in pyridine molecule also favours increasing retention (k = 9.88), although ethyl group has a lower +I-effect in comparison with a methyl group.[46]

In a series of aniline derivatives (see Fig. 2, *b*), at a ratio of MeCN : H_2O = 30 : 70, the retention increases in the order: acetonilide (retention factor k = 2.72) < aniline (k = 2.74) < 4-methylaniline (k = 2.89) < *N*,*N*-dimethylaniline (k = 5.58) < 1,4-diaminobenzene (k = 19.15) <

Table 2. Correlation equation for dependencies of logarithm of retention factor on physicochemical characteristics of nitrogen-containing aromatic compounds*

Correlation equation	R^2	r	s_b
Aniline derivatives			
$\ln k = 1.353 - 0.239\mu$	0.825	0.908	0.155
$\ln k = 1.268 - 0.277\mu + 0.005\alpha$	0.828	0.910	0.128
$\ln k = 0.605 - 0.211\mu + 0.060\alpha - 0.184\lg P$	0.993	0.997	0.043
$\ln k = -0.114 - 0.075\mu + 0.085\alpha - 0.252\lg P + 0.059pK_{BH^+}$	0.996	0.998	0.050
Pyridine derivatives			
$\ln k = 2.185 - 0.695\mu$	0.623	0.789	0.189
$\ln k = 3.238 - 0.806\mu - 0.025MR$	0.850	0.898	0.137
$\ln k = 2.883 - 0.716\mu + 0.016pK_{BH^+} - 0.022MR$	0.875	0.925	0.104
$\ln k = 3.298 - 0.659\mu + 0.037pK_{BH^+} - 0.062MR + 0.498\lg P$	0.975	0.984	0.081

* Mobile phase composition MeCN : H_2O = 70 : 30 vol.%; here and in Table 3, R^2 is correlation coefficient, r is numerical correlation coefficient, s_b is standard deviation (standard error).

< *N*,*N*,*N*′,*N*′-tetramethyl-*p*-phenylenediamine ($k = 56.29$). Acetanilide retention is the lowest in a series of the considered compounds refered to above. The reason is a high polarity of its molecule ($\log P = -0.29$, $\mu = 2.87$ D). Introduction of methyl group to *para*-position in aniline increases the hydrophobicity of 4-methylaniline ($\log P = 0.94$, $\mu = 1.48$ D for aniline and $\log P = 1.39$, $\mu = 1.27$ D for 4-methylaniline) as well as favours its sorption on the surface of UDD. Substitution of hydrogen atoms by methyl groups in amino group of aniline results in a higher increase of retention of *N,N*-dimethylaniline which is related to a reduced polarity of the compound ($\log P = 2.31$, $\mu = 1.58$ D). Retention values of 1,4-diaminobenzene and *N*,*N*,*N*′,*N*′-tetramethyl-*p*-phenylenediamine are the highest among the studied aniline derivatives as these molecules have the lowest dipole moment. Those for 1,4-diaminobenzene and *N*,*N*,*N*′,*N*′-tetramethyl-*p*-phenylenediamine are 0.02 and 0.05 D respectively. These dependencies show that at a ratio of MeCN : H_2O = 30 : 70 an the increase in retention of aniline derivatives occurs when dipole moment of a molecule decreases.

It is known that non-specific intermolecular interactions are defined mainly by the molecule volume and by such characteristics depending on the molecule volume, as polarizability and molecular refractivity.[33] At a ratio of MeCN : H_2O = 30 : 70 and the column temperature of 45 °C the correlation dependencies between the retention and the characteristics outlined above were obtained. The correlation coefficients are shown in Table 3.

The presented data indicate that the retention increases with decreasing dipole moment and increasing values of acid capacity and polarizability of the sorbate molecules. It seems reasonable to suggest that the increasing polarizability favours the ability of molecule to enter into dispersion interactions with the stationary phase.

We verified the possibility of using the derived correlation equations to estimate (predict) chromatographic retention of different structure analogues of aniline. Except for 4-methylaniline, the correlation equation was calculated for aniline derivatives applied in this work. The following correlation was obtained: $\ln k = 0.689 - 0.216\mu + 0.054\alpha - 0.172\log P$. The correlation coefficient was found to be $R^2 = 0.998$. This value was further applied to calculate the retention factor for 4-methylaniline. The difference between the theoretical value (2.35) and the experimental result (2.49) was 7%.

Among the investigated compounds a certain merit deserves *N*,*N*-dimethyl-4-aminopyridin as its molecule includes both heterocyclic and amino group. The combined effect of these structural fragments leads to a stronger increase in the retention of this sorbate in comparison with the other compounds studied (see Fig. 2, *b*). When MP with a high content of acetonitrile is used the retention of *N*,*N*-dimethyl-4-aminopyridin increases due to a high basicity of the molecule ($\ln k = 5.34$ at MeCN : H_2O = 70 : 30). When MP with a small content of acetonitril is used its retention grows owing to high electron density of pyridine ring, that is caused by the presence of two methyl groups ($\ln k = 5.98$ at MeCN : H_2O = 35 : 65).

The influence of temperature on nitrogen-containing aromatic compound on UDD. In this study adsorption of a series of aniline and pyridine derivatives on UDD surface in a temperature range 45–65 °C was investigated and a set of $\ln k = f(T^{-1} \cdot 10^3)$ plots was obtained (Fig. 3).

According to the data presented in Fig. 3 for MP with a high acetonitrile content increase in temperature causes gradual decrease in retention values for all sorbates except for the voluminous flat molecules of indole, pyridine and quonoline. Their retention factors increase with increasing temperature (see Fig. 3, *a*). It is possible, in particular, that MP contains a component with a high sorption activity and at low temperatures the molecules of this component blocks the strongest active stiles on the surface of a polar sorbent. In this case weakly polar molecules cannot withdraw strongly adsorbed species. With increasing temperature specific interactions decrease and volumetric molecules of the indole, quonoline and pyridine are already able to force the molecules of hyghly

Table 3. Correlation equations for dependencies of logarithm of retention factor on physicochemical characteristics of nitrogen-containing aromatic compounds*

Correlation equation	R^2	r	s_b
Aniline derivatives			
$\ln k = 3.463 - 1.032\mu$	0.684	0.827	0.221
$\ln k = 0.367 - 0.736\mu + 0.178\alpha$	0.934	0.967	0.116
$\ln k = 1.363 - 1.151\mu + 0.193\alpha - 0.547\lg P$	0.976	0.988	0.109
$\ln k = -4.950 - 0.046\mu + 0.435\alpha - 0.677\lg P + 0.284\mathrm{p}K_{BH^+}$	0.979	0.989	0.097
Pyridine derivatives			
$\ln k = 8.517 - 3.404\mu$	0.857	0.926	0.353
$\ln k = 7.309 - 2.8696\mu + 0.062\mathrm{p}K_{BH^+}$	0.887	0.942	0.206
$\ln k = 9.055 - 3.051\mu - 0.037\mathrm{M}R + 0.034\mathrm{p}K_{BH^+}$	0.922	0.960	0.103

* Mobile phase composition MeCN : H_2O = 30 : 70 vol.%.

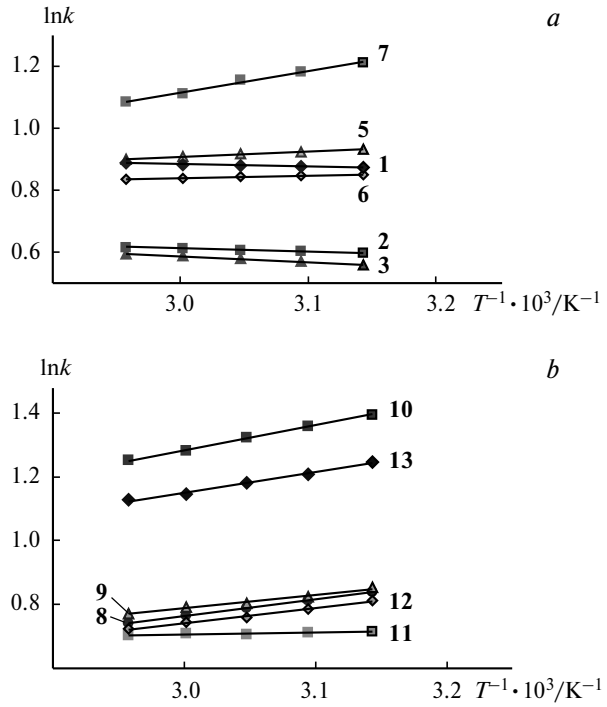


Fig. 3. Dependence of ln$k$ on $T^{-1}\cdot 10^3$ at MeCN : H_2O = = 70 : 30 for pyridine **1**—**3**, **5**—**7** (*a*) and aniline **8**—**13** (*b*) derivatives.

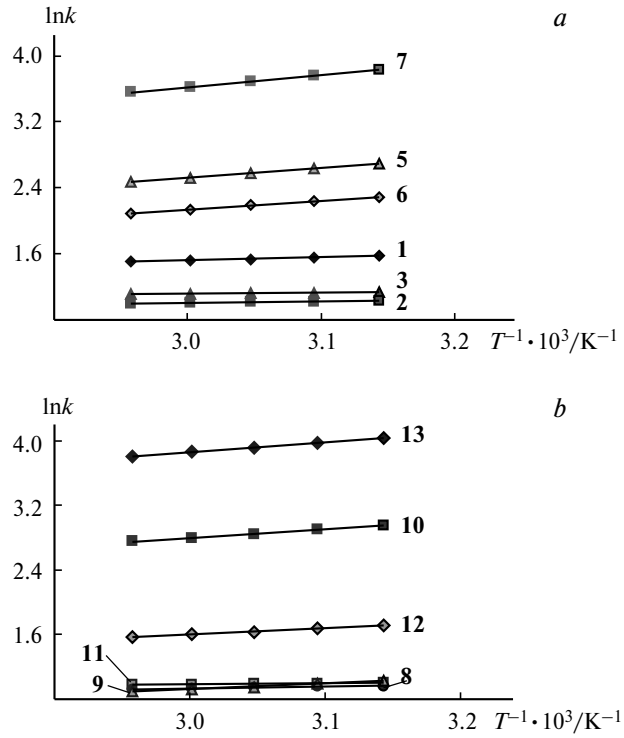


Fig. 4. Dependence of ln$k$ on $T^{-1}\cdot 10^3$ at MeCN : H_2O = = 30 : 70 for pyridine **1**—**3**, **5**—**7** (*a*) and aniline **8**—**13** (*b*) derivatives.

sorptive component out and to sorb on the UDD surface due to higher dispersion interaction.[47]

With reduced acetonitrile mole fraction in MP, the plot $\ln k = f(T^{-1}\cdot 10^3)$ changes, and with acetonitrile content lower than 40 vol.% the slopes of the plots become similar for all the sorbates and reasonable decrease of retention occurs with increasing temperature (Fig. 4).

The linear dependencies between the logarithm of retention factor (provided the relation MeCN : H_2O = = 30 : 70; 40 : 60; 50 : 50; 60 : 40; 70 : 30) and column temperature (in a temperature range 45—65 °C) were obtained with high correlation coefficients (0.987—0.998). Based on the obtained plots the thermodynamic parameters of the competitive sorption of a series of aniline and pyridine derivatives on UDD were calculated (Table 4).

The data presented in Table 4 show that enthalpy and entropy factor calculated from $\ln k = f(T^{-1}\cdot 10^3)$ plots change symbatically. At the same time the change of ΔH and ΔS as a function of MP composition has a complicated pattern. This is likely to be related to different intermolecular interactions and varying contributions of enthalpy and entropy in adsorption.

As follows from the Table 4, an increase in volume content of acetonitrile in MP from 40 to 50% leads to reduced $|\Delta H|$ for most of sorbates studied. It seems to be related to increasing energy needed to displace acetonitrile molecules from the UDD surface to the bulk solution. Another reason can be an increase in solvation of polar molecules of the sorbate with an increase in organic modifier content in MP.[48,49] Futher increase in the acetonitrile content from 50 to 60 vol.% leads to enhanced values of $|\Delta H|$, caused by the mechanism of sorbate retention change (50 vol.% is minimum point, see Fig. 2). At the same time the growth of $|\Delta S|$ is observed. Displacement of molecules of the organic modifier from the adsorption layer to the bulk solution provides the appearance of additional degree of freedom that results in the entropy factor growth. Some reduction in $|\Delta H|$ values under acetonitrile concentration of 30 and 70 % compared with 40 and 60 vol.% is likely due to energy rise needed to displace molecules of MP from the sorbent surface.

We have detected the occurrence of the thermodynamic compensation effect, which is expressed by the linear dependence of ΔH on ΔS and proves similar nature of physicochemical processes in the considered sorption systems (Fig. 5).[50,51] Thermodynamic compensation effect involves the changes of equilibrium constants of similar processes that result from the change of ΔH which are partly compensated by the corresponding changes in ΔS.[52]

Compensation effect is expressed by Eq. (9)[33]

$$\Delta H = \beta\Delta S + \Delta G_\beta, \qquad (9)$$

where ΔG_β is the change of free energy of interaction at compensation temperature β.

As it is shown in Fig. 5, for different types of sorbates the slope of dependence between the change of sorption enthalpy ΔH and the change of sorption entropy ΔS

Table 4. Changes of thermodynamic values of enthalpy (ΔH) and entropy (ΔS) for competitive adsorption of applied sorbates on UDD

Sorbate	MeCN : H_2O (vol.%)	$-\Delta H$ /kJ mol^{-1}	ΔS /J mol^{-1} K^{-1}
1	30 : 70	1.0±0.03	18.7±0.67
	40 : 60	3.2±0.43	10.7±0.46
	50 : 50	1.3±0.05	16.1±0.57
2	30 : 70	1.0±0.02	16.6±0.64
	40 : 60	2.4±0.04	11.6±0.22
	50 : 50	−0.3±0.05	19.4±0.76
	60 : 40	1.1±0.02	21±1.1
	70 : 30	−0.9±0.14	19.5±0.66
3	30 : 70	0.4±0.11	19.3±0.18
	40 : 60	2.7±0.05	10.7±0.54
	50 : 50	0.2±0.01	17.5±0.31
	60 : 40	−1.2±0.02	20.6±0.39
	70 : 30	−1.7±0.03	21.5±0.93
5	30 : 70	9.5±0.57	−5.5±0.77
	40 : 60	5.2±0.29	8.0±0.41
	50 : 50	3.2±0.12	11.1±0.58
	60 : 40	3.1±0.28	9.7±0.71
	70 : 30	1.3±0.04	15.4±0.61
6	30 : 70	9.2±0.08	−5.3±0.06
	40 : 60	3.8±0.13	10.5±0.35
	50 : 50	2.4±0.15	12.2±0.25
	60 : 40	1.2±0.07	15.2±0.84
	70 : 30	0.7±0.02	16.6±0.56
7	30 : 70	9.9±0.39	−5.2±0.38
	40 : 60	11.6±0.61	−13.0±0.54
	50 : 50	3.5±0.30	12.4±0.43
	60 : 40	7.2±0.67	0.3±1.24
	70 : 30	5.9±0.16	3.5±0.63
8	30 : 70	1.4±0.24	15.4±0.76
	40 : 60	3.1±0.12	9.4±0.47
8	50 : 50	2.1±0.11	11.9±0.52
	60 : 40	2.1±0.15	11.6±0.64
	70 : 30	4.3±0.17	5.2±0.21
9	30 : 70	2.8±0.16	11.1±0.74
	40 : 60	3.5±0.08	8.5±0.32
	50 : 50	2.6±0.12	11.0±0.52
	60 : 40	1.5±0.17	13.5±0.81
	70 : 30	3.5±0.13	7.9±0.53
10	30 : 70	9.9±0.32	−3.6±0.16
	40 : 60	19.1±0.44	−35±1.7
	50 : 50	4.1±0.21	10.9±0.67
	60 : 40	9.5±1.04	−5.8±0.52
	70 : 30	6.5±0.47	3.0±0.13
11	30 : 70	1.3±0.08	16.7±0.25
	40 : 60	1.1±0.04	15.0±0.57
	50 : 50	−0.6±0.05	20.2±0.65
	60 : 40	−0.6±0.08	19.6±0.51
	70 : 30	0,3±0,07	16.2±0.35
12	30 : 70	5.1±0.14	5.7±0.72
	40 : 60	3.4±0.08	8.9±0.44
	50 : 50	2.9±0.11	9.3±0.58
	60 : 40	1.5±0.15	13.5±0.61
	70 : 30	3.9±0.37	6.2±0.33
13	30 : 70	6.8±0.25	1.6±0.68
	40 : 60	10.1±0.28	−10.1±0.71
	50 : 50	3.1±0.16	14.7±0.45
	60 : 40	5.9±0.27	4.5±0.19
	70 : 30	5.4±0.21	5.3±0.11

remains constant that confirms the idea of similar sorption mechanism of different sorbates provided that the MP composition remains the same.

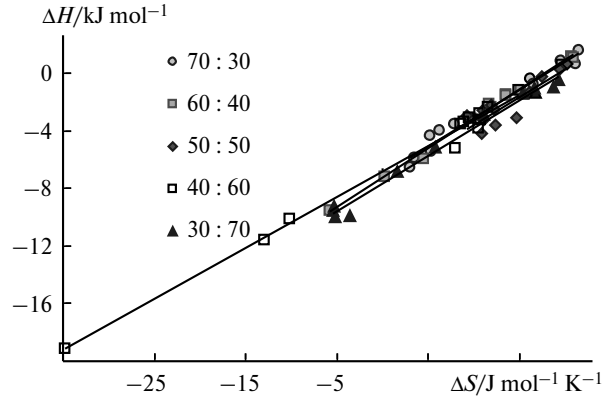


Fig. 5. Correlation between the change of enthalpy (ΔH) and the change of entropy (ΔS) for competitive sorption of aniline and pyridine derivatives on UDD at various volume ratio MeCN : H_2O.

Thus, the influence of different functional groups in molecules of nitrogen-containing compounds of pyridine and aniline derivatives on their retention on the UDD surface was investigated. Introduction of electro-donating substitutions to the molecule of the sorbate was found to decrease its retention. The non-linear relationship between retention and concentration of the organic modifier in MP was observed. The obtained dependences were described by a parabolic curve with a minimum. Such behavior can be attributed to the change of accessibility of polar and non-polar active centers on the UDD surface caused by variation of acetonitrile fraction in MP. The change in accessibility of active centers results in different contribution of specific and non-specific interactions to the retention of the model sorbates on the UDD surface. Good correlations were observed between retention of aniline and pyridine derivatives and molecule properties such as dipole moment and polarizability provided different MP compositions. Moreover, the best correlations for aniline derivatives were obtained when the lipophilicity index was accounted for and those for pyridine derivatives

when the acid capacity was included. The relation between enthalpy or entropy factor and MP composition was found to be complicated due to the competitive character of intermolecular interactions as well as different contribution of enthalpy and entropy in sorption of multicomponent systems.

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