Investigation of adsorption of phenols on detonation nanodiamonds using liquid column chromatography

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ABSTRACT

Adsorption of phenols on microdisperse sintered detonation nanodiamond (MSDN) from water–acetonitrile solutions was investigated using high performance liquid chromatography (HPLC). Parabolic dependence between retention and organic solvent content in mobile phase was observed. The influence of physicochemical characteristic solutes including molecular volume (V), dipole moment (μ), hydrophobicity (logP), polarizability (α) and molecular refractivity (MR)) of phenols on their adsorption from water–acetonitrile solutions was investigated. Single- and multi-parameter correlations between retention factor and various physicochemical characteristics of sorbates were obtained. The effect of column temperature on adsorption of phenols on UDD was investigated. The changes in ΔH and ΔS for competitive adsorption of the test sorbates were determined.

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1. Introduction

Sorptive pre-concentration also known as solid phase extraction (SPE) of various organic compounds from diluted solutions is a popular sample preparation method in trace analysis of priority pollutants. As a rule, the introduction of a new adsorption material for SPE considers the basic optimization of pre-concentration conditions for target compounds, but detailed study of adsorption properties of packing materials is missing. Correspondingly, physicochemical characteristics of adsorption and adsorbents are not properly investigated, that limited possible use of SPE adsorbent in other applications. Currently, the most popular SPE adsorbents for organic compounds are hydrophobic octyl- and octadecyl silica gels and poly(styrene-divinylbenzene) polymers [1–4]. However, these adsorbents are ineffective for pre-concentration of polar organic compounds in particular phenols, so there is a strong demand for new selective and efficient adsorbents.

Phenol and its derivatives are considered as priority pollutants of environment and their content in waters is strictly regulated by US (EPA) [5,6] and European Union [7] Environmental Protection agencies. SPE is one of effective methods for pre-concentration of phenols. The application of various adsorbents including alkylsilica [8,9], activated carbon [10], graphene [11], poly(styrene-divinylbenzene) [12], activated carbon [13,14], and graphite [15] has been reported. Recently, the use of nanocarbon materials and composites on their basis attracted strong interest of researchers as a possible alternative to traditional adsorbents. Nanocarbon materials such as carbon nanotubes (CNT) [16–18], fullerenes [19] and graphene/graphene oxide [20–22] have excellent mechanical stability, no swelling in organic solvents, hydrolytic stability, high adsorption capacity due to the developed surface area and exhibit high selectivity towards phenols.

Recently, the possibility of using detonation nanodiamond (DND) based adsorbents for selective pre-concentration and chromatographic separation was demonstrated [23–28]. According to literature data [24,25] DND particles of average size 3–5 nm and specific surface area 300–400 $m^2 \cdot g^{-1}$ consist of diamond nucleus and external sp^2 carbon shell containing various functional groups (hydroxylic, carboxylic etc.) at the surface. Thus, DND can be considered as low-polarity adsorbent, capable of both specific interactions and non-specific interactions. However, the use of fine DND particles is impractical for both SPE and chromatography because of enormous cartridge/column backpressure, so various aggregated forms and DND composites including microdisperse sintered detonation nanodiamond (MSDN) are considered. MSDN has particles size in the range from 1 to 30–50 μm, specific surface area 170–190 $m^2 \cdot g^{-1}$ and after fractionation can be used in SPE and high performance liquid chromatography (HPLC) [24,25,29]. The technique of sintering and characteristics of the obtained sintered diamonds were described in [30].

When used as a sorption system polar adsorbents (in this case the sintered nanodiamonds) and polar eluents (water–organic) the so-called hydrophilic chromatography mode is implemented. In this case we use water–organic eluents with a high content of organic modifier (greater than 70%), usually as methanol or acetonitrile, to provide a highly hydrophilic interaction between sorbates and the sorbent

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surface. The main advantage of the hydrophilic chromatography is a highly selective separation of polar compounds. The three most commonly used mobile phase modifiers significantly different selectivity: acetonitrile (ACN), methanol (MeOH) and tetrahydrofuran (THF). In this paper we investigated the adsorption of phenol derivatives using a water–acetonitrile solution. Acetonitrile belongs to VI group of separation selectivity capable mainly to the dipole–dipole interaction of the Snyder triangle selectivity.

The application of MSDN has been reported for the preconcentration of azo dyes [31], proteins [32], drugs [33,34], mycotoxins [35], inorganic ions [36], as well as in gas chromatography (GC) [37] and HPLC [38–41]. Also, there are studies on adsorption properties of DND modified by metal nanoparticles [42]. The goal of the present study is investigation of physico-chemical regularities of adsorption of a series of phenols on MSDN by using HPLC.

2. Experiment

2.1. Chromatographic system

The study was conducted using HPLC instrument Shimadzu LC-20 Prominence (Shimadzu, Japan) composed of two high-pressure pumps and spectrophotometric detector Shimadzu SPD-10Avp ($\lambda =$ 190–370 nm). Stainless steel chromatographic column 50 × 4.6 mm packed with UDD was used. The isolated fraction of UDD («ALIT», Kiev, Ukraine) contained the particles of diameter of 3.5–4.5 μm with specific surface of 191 m^2/g and effective average pore diameter of 4 nm.

2.2. Reagents and solvents

HPLC grade acetonitrile, (Panreac, Spain), ethanol 96% (Reahim), deionized water (deionizer Portlab D-301) were used. MP was prepared without the use of buffer solutions. When conditioning the column with a mobile phase of water–acetonitrile pH was 7. The solutions of hydroquinone, resorcinol, pyrocatechol, p-aminophenol, o-aminophenol, m-nitrophenol, o-nitrophenol, p-nitrophenol (Sigma-Aldrich, USA) in mobile phase were used as model compounds. Some physicochemical characteristics of these compounds [43,44] are listed in Table 1.

3. Results and discussion

The adsorption of model compounds was investigated in dynamic mode using standard HPLC equipment and short chromatographic column packed with 3.5–4.5 μm MSDN particles. It allowed simplification and intensification of the experiments on characterization of adsorption properties of MSDN.

In this work the adsorption properties of polar adsorbent UDD are studied using liquid chromatography with polarity of eluents varied in a broad range. The three solvents for liquid chromatography, which are fully mixable with water, include acetonitrile (ACN), methanol and tetrahydrofuran. However, the use of the acetonitrile is preferable here because of lower viscosity of its mixtures with water and more profound effects for aprotic solvents in the so-called hydrophilic interaction chromatography (HILIC) mode.

3.1. The influence of the mobile phase composition on the retention of phenols

At the first step of the investigation the retention of phenol on a column packed with MSDN was evaluated in water–acetonitrile mobile phase with varied content of organic solvent. The corresponding plots (Figs. 1–2) of logarithm of retention factor (ln$k$) versus mole fraction of acetonitrile in mobile phase have distinctive non-symmetrical parabolic type with minimum at $X_{CH3CN} = 0.659$ ($X_{CH3CN} = 0.705$ for pyrocatechol). At low acetonitrile content $X_{CH3CN} = 0.355–0.659$ the retention of phenols decreases continuously, but further increase of acetonitrile content in mobile phase cause substantial increase of ln$k$.

Obviously, such retention behavior is due to changes in retention mechanism, which is associated with competitive adsorption of phenols and water molecules [45,46]. In highly polar mobile phases with low acetonitrile content the molecules of water are competing strongly

Table 1
Structure and physico-chemical properties of selected phenols (M_r — molecular mass, g/mol; pK_a — acid value of the compounds; logP — logarithm of distribution factor in the system n-octanol–water; μ — dipole moment of the molecule, D; α — molecule polarizability, Å^3; V — molecular volume, Å^3; MR — molecular refractivity, mol/cm^3) [43,44].

Name	Structure	M_r, g/mol	pK_a[a]	LogP	μ, D [44]	α, Å^3	V, Å^3	MR, mol/cm^3
Phenol		94.11	9.79	1.46	1.40	11.07	352.38	27.75
Pyrocatechol		110.10	9.26	0.88	2.58	11.71	371.81	29.45
Resorcinol		110.10	9.20	0.80	1.53	11.71	373.57	29.45
Hydroquinone		110.10	9.85	0.59	0	11.71	374.01	29.45
o-Aminophenol		109.14	9.87	0.62	1.86	12.42	385.06	32.45
p-Aminophenol		109.14	10.45	0.04	2.49	12.42	387.09	32.45
o-Nitrophenol		139.12	7.04	1.79	3.10	12.91	410.47	35.08
m-Nitrophenol		139.12	8.16	2.00	3.90	12.91	413.77	35.08
p-Nitrophenol		139.12	6.96	1.91	5.05	12.91	413.47	35.08

[a] Table 1 shows the values of acidity constants criteria on the premise that the molecules of phenolic derivatives dissociate completely, as the values of acidity constants are low. In case of aminophenols we consider the values of acidity constants on hydroxyl group, as we investigate the retention dependence of the compounds on the molecules acidity, i.e. on capacity for acidic dissociation of OH-group.
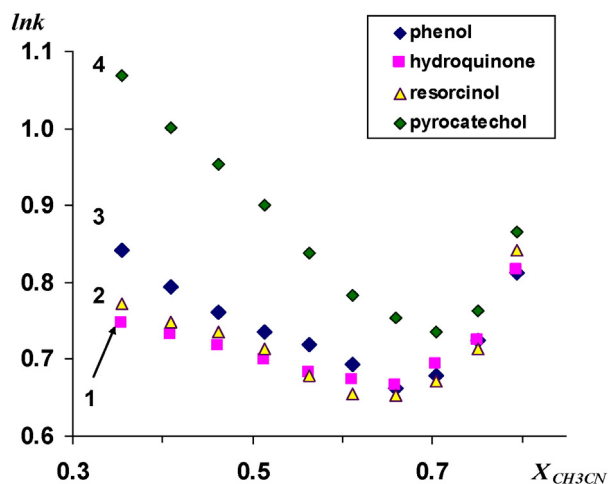
Fig. 1. Dependence of ln$k$ on mole fraction of acetonitrile in the mobile phase. Solutes: 1 — resorcinol, 2 — hydroquinone, 3 — phenol, 4 — pyrocatechol.

with phenol molecules for interaction with hydrophilic adsorption sites (hydroxy- and carboxyl-groups) at MSDN surface [47]. Under these conditions phenols are mainly retained due to non-specific intermolecular interactions. With increase of the content of acetonitrile in mobile phase from 30 to 60 vol.% the concentration of acetonitrile molecules at the surface of stationary phase increases and competition between phenols and acetonitrile molecules increases for the hydrophobic cites of at the surface of MSDN [48,49].

However, the retention order p-nitrophenol (1.91) < o-nitrophenol (1.78) < m-nitrophenol (2.00) < resorcinol (0.80) < hydroquinone (0.59) < phenol (1.46) < pyrocatechol (0.88) < o-aminophenol (0.62) < p-aminophenol (0.04) obtained for mobile phases with $X_{CH3CN} = 0.355$ does not fully correlated to the hydrophobicity (logP are presented in brackets) of these compounds. Obviously, the effect of other parameters should be considered to understand the retention mechanism. These parameters may include electron density in a benzene ring, which depends on the type and number of substitutes (electron-donor or electron-acceptor), polarizability of solute, molecule size and configuration affecting its orientation relative to the adsorbent surface, shielding of polar functional groups by non-polar groups and formation of an intramolecular hydrogen bonds between adjacent polar functional groups.
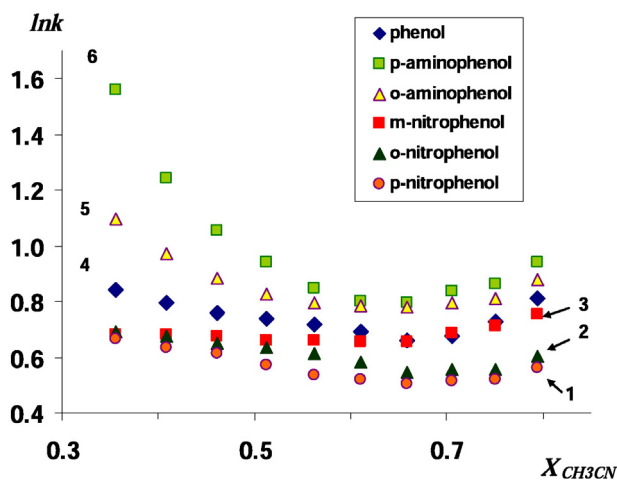
3.2. Normal-phase chromatography in water-containing eluents

The above mentioned effects have more profound effect in the retention of organic molecules under conditions of normal-phase chromatography, e.g. for MP with high concentration of acetonitrile ($X_{CH3CN} > 0794$). In this case the retention of phenolic compounds depends mainly on specific intermolecular interactions of the molecules with the polar groups at the surface of diamond. In a series of dihydroxybenzenes the retention increases in the row resorcinol < hydroquinone ~ phenol < pyrocatechol (Fig. 1). The presence of two hydroxyl groups in the molecules of resorcinol and hydroquinone results in the weaker retention as compared with phenol, which illustrates an acidic nature of carboxyl and hydroxyl groups on UDD surface. The obtained retention order $meta$ < $para$ corresponds to the higher acidity of phenolic groups in resorcinol (pK$_a$ = 9.20, see Table 1) as compared with hydroquinone (pK$_a$ = 9.85). A stronger retention of pyrocatechol having relatively acidic phenolic group (pK$_a$ = 9.26) occurs due to formation of intramolecular hydrogen bonding between two OH-groups located in $ortho$-position in the benzene ring.

Introduction of amino group to the phenol molecule results in increase of the retention due to electrostatic interactions between protonated aminophenols and negatively charged UDD surface. The retention of $ortho$-isomer is weaker than retention of $para$-isomer due to strong intermolecular bonding between hydroxyl and amino groups, which effects on interaction amino-group and UDD.

The presence of electron-acceptor nitro-groups in phenol molecules increases acidity of phenols (Fig. 2), which weakens interaction of these sorbates with UDD surface. As a results the retention of nitrophenols increases in a row p-nitrophenol (pK$_a$ = 6.96) < o-nitrophenol (pK$_a$ = 7.04) < m-nitrophenol (pK$_a$ = 8.16) < phenol (pK$_a$ = 9.79). Clearly, nitro-substitute reduces the electron density in benzene ring influencing electron pair at oxygen that results in weakening of O–H bond [50]. Again, o$rtho$-nitrophenol is retained stronger than $para$-isomer because of intramolecular interaction between hydroxyl and nitro groups [51], reducing the dissociation degree of phenol group. $Meta$-nitrophenol has a special place in the series as nitro-group draws the electron density from benzene ring, but at the same time hydroxy-group is not involved in redistribution of electron density. This reduces dissociation degree of phenol group and does not effecting strongly on the retention as compared to phenol [50].

There are two possible retention mechanisms including either adsorption or partition under the conditions of hydrophilic interactions liquid chromatography (HILIC) or normal-phase liquid chromatography in water-containing mobile phases. To determine the dominant

Fig. 2. Dependence of ln$k$ on mole fraction of acetonitrile in the mobile phase. Solutes: 1 — p-nitrophenol, 2 — o-nitrophenol, 3 — m-nitrophenol, 4 — phenol, 5 — o-aminophenol, 6 — p-aminophenol.
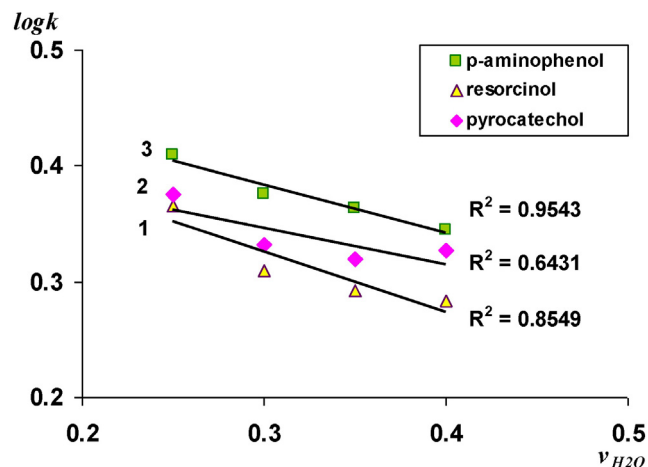

Fig. 3. The dependence of logarithm of retention factor of phenolic derivatives on UDD on water content in MP. Solutes: 1 — resorcinol, 2 — pyrocatechol, 3 — p-aminophenol.
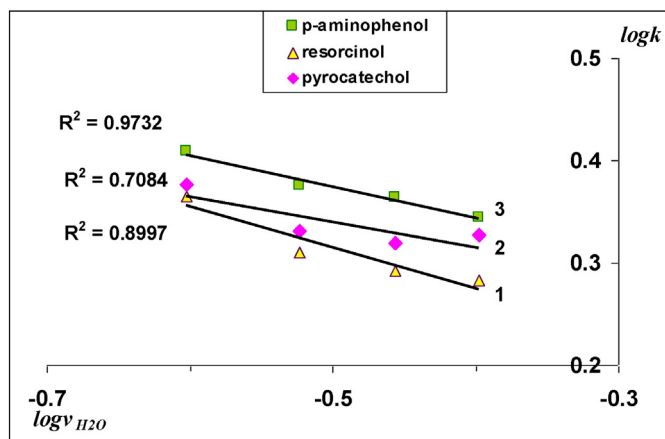
Fig. 4. The dependence of logarithm of retention factor of phenolic derivatives on UDD on logarithm of water content in MP. Solutes: 1 — resorcinol, 2 — pyrocatechol, 3 — p-aminophenol.

retention mechanism the correlation coefficients R^2 for linear dependencies log $k–\nu_{H2O}$ and log $k–$log ν_{H2O} obtained for selected analytes are compared. The corresponding dependencies for retention of resorcinol, pyrocatechol and p-aminophenol in mobile phases containing more than 60% of acetonitrile are shown in Fig. 3 and Fig. 4. As R^2 values for log $k–$log ν_{H2O} dependences are higher for all compounds than those calculated for log $k–\nu_{H2O}$, it was concluded that the dominant retention mechanism is associated with adsorption of these analytes [52].

Consider features of retention of certain phenolic derivatives on the most commonly used sorbents. Since the surface of nanodiamond particles contain functional groups (hydroxyl, carboxyl, etc.), DND can be considered as weakly polar adsorbent capable of both specific and nonspecific interactions.

Sorbates retained on the surface of the sorbent are primarily due to non-specific interactions in RP-HPLC. One of the non-polar adsorbents used in chromatography is porous graphite. Retention factors of some phenols on the surface of the porous graphite (PGC) [53] and nanodiamond (UDD) are shown in Table 2.

The data in Table 2 show that retention of phenol isomers increases in the following row: $p < o < m$. Retention increases in order of increasing pKa molecules of sorbates. However, on the surface of nanodiamond retention of nitrophenols lowers, which can be explained by the presence of acid groups on the surface of the sorbent. Sorption resorcinol and o-aminophenol at the UDD surface are higher than on the porous graphite. This can probably be explained by the increase of molecular interaction between sorbates and sorbent due to the formation of hydrogen bonds. Furthermore, according to [54] retention of phenols on the porous graphite (when used as a mobile phase acetonitrile–water and methanol–water) monotonically decreases. The dependence of logarithm of retention factor of the mole fraction of modifier passes through a minimum on the UDD (see Figs. 1, 2), which can be explained by a change contribution in the retention of specific and nonspecific interactions.

On the other hand, the presence of polar groups on the surface of the UDD can be attributed to a weakly polar sorbent used in the NP-HPLC. In [8] studied the adsorption of phenolic compounds on silica gel in the

NP-HPLC. As the mobile phase the authors used a mixture of n-hexane with various polar additives. The retention of nitrophenol isomers increases in the following order: $o < m < p$. o-Nitrophenol is sorbed less than other isomers by the formation of an intramolecular hydrogen bond between the OH and NO_2-groups. p-Nitrophenol is a stronger acid than the other nitrophenols, which leads to a strong polarization of the O–H bond and increase retention of p-nitrophenol by forming hydrogen bonds between hydroxyl groups on the silica surface and molecules. According to the article the increase of retention of phenol derivatives on silica surface generally can be represented by the following series: nitrophenols < phenol < aminophenols. The same sequence is increased adsorption phenols on the UDD surface.

Thus, the UDD takes an intermediate position between the nonpolar PGC and polar silica gel. This confirms our assumption of competition of specific and nonspecific interactions on the surface of the UDD.

3.3. Factors affecting retention of phenols

As shown above the acidity of phenol group can be considered as a major factor determining the retention of phenols on UDD. Fig. 5 shows the dependence of ln$k$ on acidity of phenol groups for a series of substituted phenols having values pK_a in a range 7.0–10.5 (Table 3). The retention of phenols is reciprocal to the acidity of phenol groups and strong correlation between ln$k$ and pK_a is obtained.

Apart from the pK_a values of phenolic groups the other parameters such as molecular volume (V), dipole moment (μ), hydrophobicity (logP) defined as logarithm of distribution factor in the system "n-octanol–water", polarizability (α), molecular refractivity (MR) and others (Table 1) can be used as molecular descriptors for evaluation of the effect of chemical structure of phenols on their chromatographic retention. Analysis of the corresponding parameter-retention correlations for was carried out. Correlation coefficients for some multiparameter dependences are shown in Table 3, which demonstrates that retention of phenols depends strongly not only on pK_a of sorbates but also on dipole moments and polarizability of phenol molecules.

For MPs with low content of acetonitrile ($X_{CH3CN} < 0.243$) the retention of sorbates is defined mainly by non-specific intermolecular interactions. For example, the retention of dihydroxybenzenes grows in the following row hydroquinone ($\mu = 0$, logP = 0.59) < resorcinol ($\mu = 1.53$, logP = 0.80) < pyrocatechol ($\mu = 2.58$, logP = 0.88) reflecting the growth of dipole moments and hydrophobicity of the solutes. The retention of phenol is stronger than retention of hydroquinone and resorcinol due to the absence of steric hindrance in interaction of benzene ring with UDD surface.

Introduction of amino-group to the phenol molecule increases the retention of aminophenols due to positive mesomeric effect of amino-group on electron density of benzene ring that strengthens non-

Table 2
Retention factors of some phenols on a porous graphite (PGC) and nanodiamond (UDD).

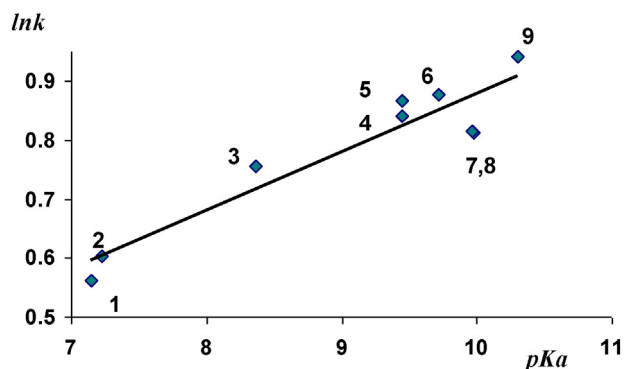| Sorbate	k_{PGC}, 70:30 CH_3OH:H_2O	k_{UDD}, 70:30 CH_3CN:H_2O
Resorcinol	1.41	2.04
o-Nitrophenol	2.64	1.75
m-Nitrophenol	3.19	2.04
p-Nitrophenol	1.94	1.68
o-Aminophenol	1.72	2.25

Fig. 5. The correlation between retention factors and pK_a values of phenolic compounds obtained with mobile phase of $X_{CH3CN} = 0.794$. Solutes: 1 — p-nitrophenol, 2 — o-nitrophenol, 3 — m-nitrophenol, 4 — pyrocatechol, 5 — resorcinol, 6 — o-aminophenol, 7 — hydroquinone, 8 — phenol, 9 — p-aminophenol.

Table 3
Correlation equations for the investigated phenols (MP composition: CH₃CN:H₂O 70:30% *v/v*).

Correlation equations	R²
$\ln k = 0.002 + 0.079 pKa$	0.851
$\ln k = -0.247 + 0.103 pKa + 0.027\mu$	0.910
$\ln k = -0.773 + 0.107 pKa + 0.016\mu + 0.040\alpha$	0.935

specific interactions of phenols with UDD surface. However *o*-aminophenol retains weaker than *para*-isomer due to strong intramolecular interaction between hydroxy- and amino-groups. Introduction of electron-acceptor nitro-groups to the phenol molecule leads, in turn, to decrease in retention of these sorbates due to reduced electron density in a benzene ring. Non-specific intermolecular interactions are defined mainly by the molecule volume and related characteristics such as polarizability and molecular refractivity [55].The high values of calculated correlation coefficients (Table 4) for corresponding multi-parameter dependences confirm the important role of these characteristics in retention of phenols on UDD.

As expected for moderately hydrophobic UDD [25,56] the retention of phenols increases with increase of logP, molecular volume and polarizability. The retention of highly polarizable solutes is stronger due to elevated possibility of dispersion interactions of phenols with UDD surface. The obtained correlations allow the prediction of the retention times for various phenols on UDD column.

3.4. The influence of temperature on phenolic compounds sorption on ultradispersed diamond

Adsorption equilibrium in chromatographic system can be described by using basic equations of chemical thermodynamics [55]:

$$\Delta G = \Delta H - T\Delta S, \tag{1}$$

where ΔG, ΔH, and ΔS — the change of Gibbs free energy, enthalpy and entropy, relatively. The dependence between ΔG and partition constant K_c of a sorbate between mobile and stationary phases is described by the following equation [57]:

$$\Delta G = -RT \ln K_c. \tag{2}$$

At the same time, partition constant K_c is directly proportional to retention factor by assuming constancy of phase ratio φ for the selected chromatographic column as follows [57]:

$$K_c = {k}/{\varphi}. \tag{3}$$

Then the dependence of the retention factor (k) versus temperature (T) can be expressed by Van Hoff equation [55]:

$$\ln k = -\frac{\Delta H}{RT} + \frac{\Delta S}{R} + \ln\varphi, \tag{4}$$

where R is gas constant and $\varphi = V_s/V_M$, where V_S and V_M are volumes of stationary phase and mobile phase, respectively.

Table 4
Correlation equations for investigated phenols (MP composition CH₃CN:H₂O 30:70% *v/v*).

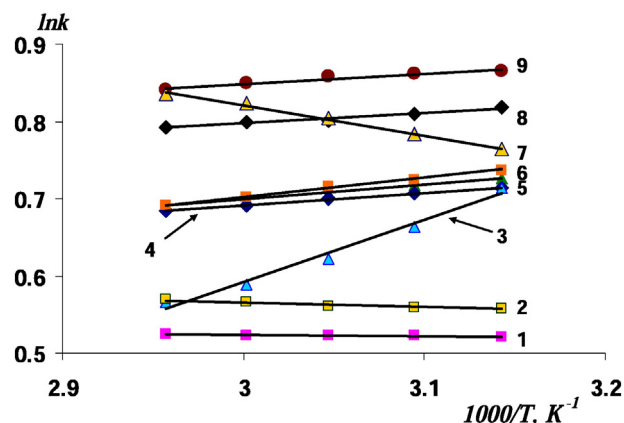| Correlation equations	R²
$\ln k = 1.240 - 0.316\log P$	0.691
$\ln k = 1.120 - 0.416\log P + 0.093\mu$	0.841
$\ln k = -0.430 - 0.276\log P + 0.143\mu + 0.143 pKa$	0.915

Fig. 6. *lnk-1000/T* plots obtained for phenols with mobile phase with acetonitrile content of $X_{CH3CN} = 0.750$ and UDD column. Solutes: 1 — *p*-nitrophenol, 2 — *o*-nitrophenol, 3 — *m*-nitrophenol, 4 — resorcinol, 5 — hydroquinone, 6 — phenol, 7 — pyrocatechol, 8 — *o*-aminophenol, 9 — *p*-aminophenol.

In this study adsorption of a series of phenols on UDD surface in a temperature range 45–65 °C was investigated and a set of $\ln k = f({1000}/{T})$ plots was obtained (Fig. 6).

It was found that increase of column temperature decreases the retention for all sorbates except of pyrocatechol and *o*-nitrophenol, when the opposite effect was observed (Fig. 6). Molecules of these sorbates have intramolecular bonding as shown in Fig. 7 [51,58], which, obviously, is sensitive to changes in the column temperature. The increase of temperatures causes breaking of intramolecular bonds and changes chemical structure, which explains such behavior of *ortho*-isomers. The slope of $\ln k - 1000/T$ plot is higher for pyrocatechol as compared with o-nitrophenol (Fig. 7). This could be connected with release of two reactive hydroxy-groups in pyrocatechol molecule after breaking intramolecular bond, while only one group can be released in case of *o*-nitrophenol.

With reduced acetonitrile content in MP the slopes of $\ln k = f({1000}/{T})$ plots are different and they become similar for all the sorbates at $X_{CH3CN} < 0462$ as shown in Fig. 8. Obviously, at higher contents of water in MP the stability of intramolecular bonding is weaker, which reduce the effect of temperature on retention of *ortho*-isomers of substituted phenols.

Based on the obtained dependences $\ln k = f({1000}/{T})$ thermodynamic parameters were calculated for adsorption of a series of phenols on UDD. The data presented in Table 5 show that calculated ΔH and ΔS change symbatically. At the same time there is no consistency in the change of ΔH and ΔS with variation of MP composition.

The thermodynamic compensation effect was found for adsorption of phenols on UDD which is expressed in occurrence of linear dependence between entropy ΔH and enthalpy ΔS of adsorption. This indicates similarity of physico-chemical processes for adsorption of selected model compounds (Fig. 9). Thermodynamic compensation effect stated that the changes of equilibrium constants of similar processes that result from the change of ΔH are partially compensated by corresponding changes in ΔS [59].
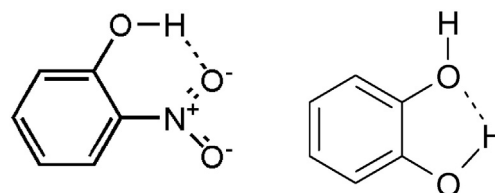

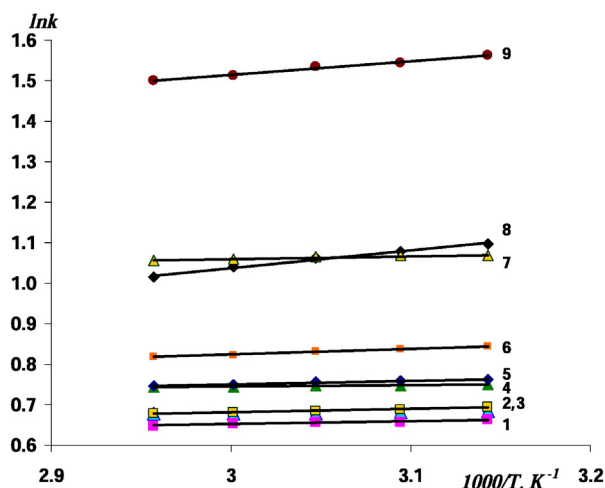Fig. 7. Intermolecular association of the molecules *o*-nitrophenol and pyrocatechol.

Fig. 8. *lnk-1000/T* plots obtained for phenols and benzoic acid with mobile phase with acetonitrile content of $X_{CH3CN} = 0.355$ and UDD column. Solutes: 1 — *p*-nitrophenol, 2 — *m*-nitrophenol, 3 — *o*-nitrophenol, 4 — hydroquinone, 5 — resorcinol, 6 — phenol, 7 — pyrocatechol, 8 — *o*-aminophenol, 9 — *p*-aminophenol.
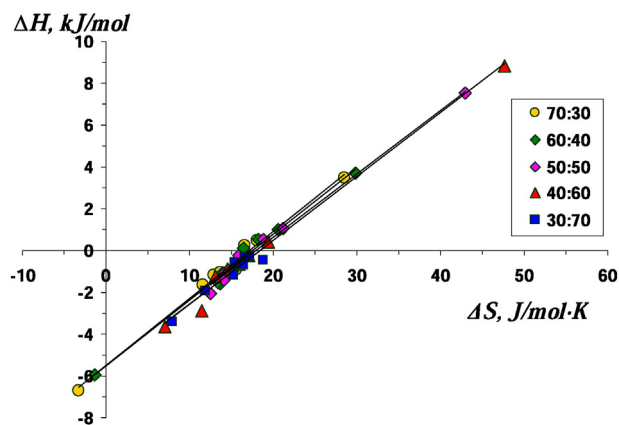

Fig. 9. Correlation between changes in ΔH and ΔS for adsorption of phenols on UDD at various compositions of MP.

Compensation effect is expressed as follows [55]:

$$\Delta H = \beta \Delta S + \Delta G_\beta, \qquad (5)$$

where ΔG_β — the change of free energy of interaction at compensation temperature β. The theory of compensation effect is based on consideration of collective phenomena in a medium that accompany elementary act of reaction, e.g. the reaction of fast and reversible reorientation of molecules in solvation shell [59]. Fig. 9 shows that for one class of sorbates the slope of dependence ΔH on ΔS is constant and consequently the change of free energy of interaction at the compensation temperature β is a constant for the considered adsorption system.

4. Conclusions

Adsorption of phenols on UDD in MP with various acetonitrile–water ratios was investigated. For all the tested sorbates parabolic type dependences of retention on organic solvent content MP composition were found, which is due to the changes in retention mechanism at high acetonitrile content associated with increased role of polar interactions between phenols and UDD surface. The influence of different physico-chemical characteristics sorbates on their adsorption from water–acetonitrile solutions was analyzed. Mono- and multiparameter dependences connecting physico-chemical properties of sorbate molecules with retention were obtained. The corresponding equations correlating the logarithms of retention factors acidity of phenol groups, lipophilicity of phenols and dipole moments are analyzed, while by strong correlation is obtained practically for all investigated adsorbates. The influence of the temperature on retention of phenols on UDD was studied. The symbatic changes in ΔH and ΔS are calculated for test sorbates and MPs with different content of acetonitrile.

Prime novelty statement

Adsorption of phenols on microdisperse sintered detonation nanodiamond (MSDN) from water–acetonitrile solutions was investigated using high performance liquid chromatography (HPLC). Parabolic dependence between retention and organic solvent content in mobile phase was observed. The influence of physicochemical characteristics solutes including molecular volume (V), dipole moment (μ), hydrophobicity (logP), polarizability (α) and molecular refractivity (MR)) of phenols on their adsorption from water–acetonitrile solutions was investigated. Single- and multi-parameter correlations between retention factor and various physicochemical characteristics of sorbates were obtained. The effect of column temperature on adsorption of

Table 5
The change of enthalpy ΔH and entropy ΔS for competitive adsorption of sorbates on UDD surface.

Sorbate	CH$_3$CN:H$_2$O, % v/v	−ΔH, kJ/mol	ΔS, J/mol·K
Phenol	70:30	1.6 ± 0.05	11.6 ± 0.55
	60:40	− 1.0 ± 0.02	20.6 ± 0.62
	50:50	− 1.1 ± 0.06	21.2 ± 0.80
	40:60	− 0.4 ± 0.02	19.3 ± 0.55
	30:70	1.2 ± 0.11	15.2 ± 0.89
Hydroquinone	70:30	1.1 ± 0.04	12.9 ± 0.67
	60:40	0.5 ± 0.02	15.8 ± 0.50
	50:50	0.5 ± 0.01	16.2 ± 0,42
	40:60	0.3 ± 0.02	17.1 ± 0.57
	30:70	0.3 ± 0.08	17.2 ± 0.12
Resorcinol	70:30	1.1 ± 0.03	13.7 ± 0.09
	60:40	1.1 ± 0.04	13.9 ± 0.54
	50:50	1.0 ± 0.01	14.2 ± 0.32
	40:60	0.6 ± 0.01	15.9 ± 0.32
	30:70	0.7 ± 0.03	16.0 ± 0.33
Pyrocatechol	70:30	− 3.5 ± 0.11	28.6 ± 0.60
	60:40	− 3.7 ± 0.06	29.8 ± 0.70
	50:50	− 7.5 ± 0.24	43 ± 1.9
	40:60	− 8.8 ± 0.12	48 ± 1.5
	30:70	0.4 ± 0.02	18.8 ± 0.80
p-Aminophenol	70:30	0.9 ± 0.06	15.6 ± 0.39
	60:40	1.6 ± 0.04	13.6 ± 0.34
	50:50	2.0 ± 0.06	12.5 ± 0.23
	40:60	2.9 ± 0.11	11.5 ± 0.24
	30:70	2.8 ± 0.05	12.0 ± 0.36
o-Aminophenol	70:30	0.9 ± 0.03	15.2 ± 0.53
	60:40	1.6 ± 0.11	13.4 ± 0.63
	50:50	1.4 ± 0.07	14.1 ± 0.38
	40:60	3.6 ± 0.09	7.0 ± 0.12
	30:70	3.4 ± 0.03	7.9 ± 0.21
m-Nitrophenol	70:30	6.7 ± 0.05	− 3.3 ± 0.07
	60:40	5.9 ± 0.03	− 1.3 ± 0.04
	50:50	0.8 ± 0.02	15.4 ± 0.49
	40:60	0.5 ± 0.03	16.2 ± 0.22
	30:70	0.3 ± 0.04	16.6 ± 0.21
o-Nitrophenol	70:30	− 0.5 ± 0.02	18.0 ± 0.72
	60:40	− 0.5 ± 0.03	18.3 ± 0.42
	50:50	− 0.5 ± 0.03	18.8 ± 0.31
	40:60	0.9 ± 0.01	14.6 ± 0.66
	30:70	0.7 ± 0.05	15.4 ± 0.40
p-Nitrophenol	70:30	− 0.2 ± 0.01	16.6 ± 0.01
	60:40	− 0.13 ± 0.004	16.4 ± 0.01
	50:50	0.25 ± 0.008	15.8 ± 0.03
	40:60	1.2 ± 0.04	13.0 ± 0.44
	30:70	0.6 ± 0.03	15.4 ± 0.42

phenols on UDD was investigated. The changes in ΔH and ΔS for competitive adsorption of the test sorbates were determined.

Acknowledgments

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