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Dedicated to I.L. Eremenko on the occasion of his 70th birthday

Influence of the Structures of the Carboxylate Porous Coordination Polymers as Stationary Phases for Liquid Chromatography on the Separation Efficiency of the Aniline Derivatives

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Abstract—The possibility of the chromatographic separation of isomeric nitroanilines and fluorine-substituted analogues using porous coordination polymers $[Al(OH)(Fum)]_n$ (**I**) (Fum^{2-} is *trans*-1,2-ethylenedicarboxylic acid anion), $[Al(OH)(Bdc)]_n$ (**II**) (Bdc^{2-} is 1,4-benzenedicarboxylic acid anion), $[Cu_3(Btc)_2(H_2O)_3]$ (**III**) (Btc^{3-} is 1,3,5-benzenetricarboxylic acid anion), and $[Cr_3(O)(OH)(H_2O)_2(Bdc)_3]$ (**IV**) as stationary phases in a mixture of nonpolar solvents is studied. The separation of the amines is achieved only in the case of $[Al(OH)(Fum)]_n$. Possible relationships of the separation factors of the amines to the sizes of the molecules, polarity, and lipophilicity are examined. Among the factors considered, only the difference between the values of lipophilicity exerts a noticeable effect on the efficiency.

Keywords: porous coordination polymers, aromatic amines, fluorine-containing organic compounds, adsorption, chromatography, lipophilicity

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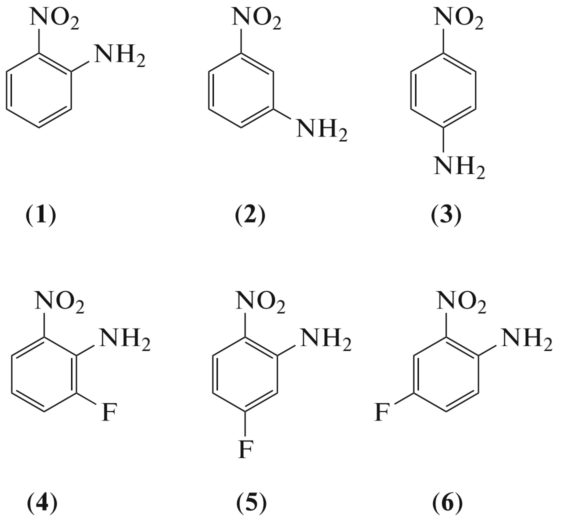
INTRODUCTION

Fluorine-containing amines are widely used as active substances in agricultural chemistry [1] and pharmaceutics [2, 3]. The separation of these amines and analogues containing no fluorine is an important task of the chemical industry, in particular, fine organic synthesis. This problem often arises when fluorine-containing anilines are synthesized by the replacement of the amino group by fluorine using the Schiemann method when a significant amount of the by-product containing the hydrogen atom at the amino group position can be formed [4]. The methods based on the crystallization of the amines or their salts and selective sorption of the amines [5] are used for the separation of these substances. In many cases, efficient separation of amine mixtures is achieved when chromatography is used [6]. One of the most important problems of the modern chemistry is the search for new adsorbents for the chromatographic separation of the fluorine-containing amines and analogues containing no fluorine and the determination of factors affecting the efficiency of the separation of these mixtures [7]. Porous coordination polymers (PCPs), whose efficiency as supports for chromatography was shown in several works [8–11], can be used as sorbents or stationary phases for chromatography.

The purpose of this work is the study of the influence of the chemical compositions and structures of the PCP on the possibility and efficiency of the chromatographic separation of isomeric nitroanilines and their fluorine-substituted analogues.

Aluminum PCPs $[Al(OH)(Fum)]_n$ (**I**) and $[Al(OH)(Bdc)]_n$ (**II**) assigned to the structural type MIL-53(Al) (Fum^{2-} is *trans*-1,2-ethylenedicarboxylic acid anion, and 1,4-Bdc^{2-} is 1,4-benzenedicarboxylic acid anion), $[Cu_3(Btc)_2(H_2O)_3]$ (**III**) known as HKUST-1 (Btc^{3-} is 1,3,5-benzenetricarboxylic acid anion), and $[Cr_3(O)(OH)(H_2O)_2(Bdc)_3]_n$ (**IV**) assigned to the structural type MIL-101(Cr) were chosen as objects of the study. The separation of the amines on silica gel Silica-60 was studied for comparison. 2-Amino-1-nitrobenzene (**1**), 3-amino-1-nitrobenzene (**2**), 4-amino-1-nitrobenzene (**3**), 2-amino-3-fluoro-1-

nitrobenzene (**4**), 2-amino-4-fluoro-1-nitrobenzene (**5**), and 2-amino-5-fluoro-1-nitrobenzene (**6**) were used as amines. Their structural formulas are presented in Scheme 1. The influence of the structures and physical properties of the studied amines and the possibility of the separation of their mixtures were examined.



Scheme 1.

EXPERIMENTAL

Commercially available reagents (Aldrich, NPP Enamine) were used without additional purification. Methyl *tert*-butyl ether for chromatography was purified to remove moisture traces by distillation over $LiAlH_4$, and *n*-hexane was used as received.

Syntheses of $[Al(OH)(Fum)]_n$ (I), $[Al(OH)(Bdc)]_n$ (II), and $[Cr_3(O)(OH)(H_2O)_2(Bdc)_3]_n$ (IV) were carried out using previously described procedures [12–14]. To remove H_2Bdc impurities, the sample of PCP **II** was heated in vacuo at 320°C for 2 days as described in [13]. The sample of PCP **IV** was consecutively washed with *N*,*N*-dimethylformamide and hot ethanol as described in [14].

For $C_4H_{11}O_9Al$			
Anal. calcd., %	C, 20.9	H, 4.82	N, 0.0
Found for **I** · $4H_2O$, %	C, 20.7	H, 4.95	
For $C_8H_8O_{6.5}Al$			
Anal. calcd., %	C, 40.9	H, 3.43	N, 0.0
Found for **II** · $1.5H_2O$, %	C, 41.1	H, 3.15	N, 0.0
For $C_{24}H_{73}O_{44}Cr_3$			
Anal. calcd., %	C, 23.6	H, 6.02	N, 0.0
Found for **IV** · $28H_2O$, %	C, 23.9	H, 5.95	N, 0.08

Synthesis of $[Cu_3(Btc)_2(H_2O)_3]$ (III) was carried out by the electrochemical dissolution of copper in a solution of H_3Btc using a modified procedure [15]: two copper plates (1.5 × 2.8 cm) were treated with 25% nitric acid for 10 s, washed with distilled water and isopropanol, and placed in a solution of NEt_4BF_4 (1.2 g) and H_3Btc (1.6 g) in 96% EtOH (50 mL) at 60°C. Electrolysis was conducted in the galvanostatic mode with a current density of 0.11–0.13 A/cm^2 (potentiostat current I = 1.4–1.5 A, voltage U = 6.0–6.5 V) for 2 h, which corresponded to 3 F/mol H_3Btc, the current source was connected according to the two-electrode scheme. The formed product was filtered off, three times washed with hot ethanol, and dried in air for 12 h and in a drying box at 80°C for 2 h. A blue powder was obtained. The yield was 1.43 g (83% based on H_3Btc).

For $C_{18}H_{12}O_{15}Cu_3$ (**III**)		
Anal. calcd., %	C, 32.8	H, 1.84
Found, %	C, 32.9	H, 1.80

The chemical purity of the synthesized compounds was checked by CHN analysis using a Carlo Erba 1106 analyzer.

The phase purity of PCPs **I**–**IV** was confirmed by X-ray diffraction analysis (XRD) on a Bruker D8 Advance diffractometer (CuK_α radiation, λ_{Cu} = 0.1542 Å). The characteristics of the porous PCP structure were determined by an analysis of the nitrogen adsorption isotherms measured at 78 K on a Sorptomatic 1990 instrument [16]. Prior to measurements, the samples were desolvated by heating at 150°C in vacuo (10^{-3} Torr).

For the separation of mixtures of nitroanilines, a glass chromatographic column 1 cm in diameter was packed with PCP **I**–**IV** at a height of 10 cm (height after PCP “ramming” under the layer of a mixture of solvents used as a mobile phase). The weight of the PCP was 9.2–9.5 g. All PCP were not desolvated before use. A methyl *tert*-butyl ether (MTBE)–*n*-hexane (70 : 30) mixture, which was passed without additional pressure, was used as a mobile phase (eluent). The adsorbent for the experiment was dispersed with ultrasound for 5 min in the mobile phase, and the suspension was poured by portions into a chromatographic column knocking it occasionally until the adsorbent height decreased to 10 cm. Before packing the chromatographic column, PCP **IV** was washed with pure MTBE under ultrasonication for 10 min. A mixture of the amines containing 1–2 mg of the substance was introduced into the column in a dichloromethane solution (50 μL) and then eluted with a MTBE–hexane mixture. The experiment was carried out in air without additional protection from moisture. The amines at the outlet of the column were identified by comparing their R_f with R_f of the standards (pure amines) for thin-layer chromatography (TLC) on silica gel Nagel using an MTBE–hexane (70 : 30) mixture as an eluent.

The lipophilicity coefficients of the studied amines (log(*P*)) were calculated using the ACD/Log P DB 10.04 program [17], and the dipole moments and sizes of the molecules were calculated by the MP2 quantum mechanics method (second-order Møller–Plesset perturbation theory) using the ORCA 4.1.2 program [18]. The def2-TZVPP basis set (as well as the def2/J and def2-TZVPP/C auxiliary basis sets for the RI [19] and COSX [20] algorithms applied for calculation acceleration) was used for the description of electron orbitals. The initial geometry of the molecule was obtained using the molecular mechanics method (MMFF94 force field, in Avogadro 1.1.1). The initial geometry was subjected to distortion (each coordinate for each atom was changed by a random value within ±0.05 Å) in order to decrease the probability of getting into the saddle point during optimization, after which the molecules were optimized by the MP2 method. The dipole moment was calculated for the equilibrium geometry also by the MP2 method (on the basis of the electron density distribution taking into account the MP2 corrections). The MP2 method was chosen due to the literature data that substantiated its sufficient accuracy for the calculation of the dipole moment [21] along with appropriate expenses of computational resources.

RESULTS AND DISCUSSION

Compounds **I**–**IV** represent 3D coordination polymers with continuous pores, being channels in the crystalline lattices [12, 13, 22, 23].

The XRD analyses of the samples as solvates equilibrated with air were carried out to determine the phase purity of PCPs **I**–**IV** and the conformations that are adopted by PCPs **I** and **II**. This approach was chosen with allowance for the fact that amine separation was studied from solutions, and the PCP were not desolvated in these experiments. The reflection positions on the obtained XRD patterns (Fig. 1) are well consistent with those expected for the PCP modifications with the parameters as follows. For PCP **I**, space group $P2_1/c$, $a = 6.842(3)$, $b = 12.088(2)$, $c = 4.21(1)$ Å, $\beta = 122.55(6)°$ [12]; for PCP **II**, space group $C2/c$, $a = 19.685(4)$, $b = 7.849(1)$, $c = 6.782(1)$ Å, $\beta = 104.90(2)°$ [24]; for PCP **III**, space group $Fm\bar{3}m$, $a = 26.2879(3)$ Å [25]); and for PCP **IV**, space group $Fd\bar{3}m$, $a = 88.869$ Å [23]. In the case of PCP **I**, the reflections are substantially broadened. For PCP **IV**, the relative reflection intensities in the range $2\theta < 12°$ are much lower than the expected values. These distinctions of the experimental XRD patterns from the calculated ones are caused, most likely, by disordering of the crystal lattices of PCPs **I** and **IV**.

The polymeric networks of PCPs **I** and **II** are labile. The structure of PCP **II** changes easily depending on the presence of guest molecules, and the pore size of this PCP can take the values from 8.5×8.5 Å^2 (PCP with unfilled pores) to 2.6×13.6 Å^2 (PCP with the trapped water molecule) [13]. The lability of the structure of PCP **I** is manifested under high pressures [26], but the presence of guest molecules exerts no substantial effect on the crystal lattice structure of this compound [12]. Nevertheless, various values of pore sizes of PCP **I** are presented in the literature: from 5.7×6.0 Å^2 [12] to 7.3×7.7 Å^2 [26]. The polymeric lattices of PCPs **III** and **IV** are conformationally rigid, and the pore sizes are 9×9 Å^2 for PCP **III** [22] and 29–34 Å for PCP **IV** [23]. These pore estimations are based on the measurement of the distances between the atoms arranged at opposite sides of the pore taking into account their van der Waals radii. A drawback of this approach is the ambiguous choice of the atoms used for estimation. According to the XRD data, PCP **I** retains the configuration with "open" pores, whereas PCP **II** adopts the "folded" conformation.

An alternative approach can be the estimation of the pore size using the PLATON software [27] from the dependence of the volume accessible for guest molecules on the diameter of the probe molecule. The pore size can be considered to be the maximum diameter of the probe molecule for which the accessible volume is not equal to zero yet. A drawback of this approach is that it does not directly estimate the size of the "window" leading to the pore and, as a consequence, the obtained pore size does not warrant its accessibility for molecules of close sizes. According to the estimation performed using the PLATON software, the pore diameter in PCP **I** is 5.5 ± 0.1 Å, and that in PCP **IV** is 30.6 ± 0.1 Å, which is well consistent with the values presented above. PCP **II** contains pores with a diameter of 3.0 ± 0.1 Å. For "unfolded" modification **II** (with the parameters: space group *Imcm*, $a = 16.772(8)$, $b = 13.145(5)$, $c = 6.847(5)$ Å [28]), the transition to which is not theoretically excluded upon nitroaniline sorption, a similar estimation gives the pore diameter at a level of 7.2 ± 0.1 Å. In the case PCP **III**, the estimation of the pore size performed using probe molecules in the PLATON software is 13.6 ± 0.1 Å, which exceeds the pore size determined as the distance between opposite atoms in the pore. This distinction can be explained by a high difference between the size of the "window" leading to the pore and the size of the cavity itself.

The characteristics of the porous structures of PCPs **I**–**IV** were determined by an analysis of the nitrogen adsorption isotherms (Fig. 2). The surface areas (S_{BET}) of the studied PCP range from 1290 to 3160 m^2/g, the micropore volume determined according to the Dubinin–Radushkevich equation (V_{DR}) ranges from 0.498 to 0.710 cm^3/g, and the total pore volume (V_{T}) ranges from 0.560 to 1.464 cm^3/g, which is comparable with the published data [12, 23, 29–31]. In the cases of PCPs **I** and **II**, the micropore size

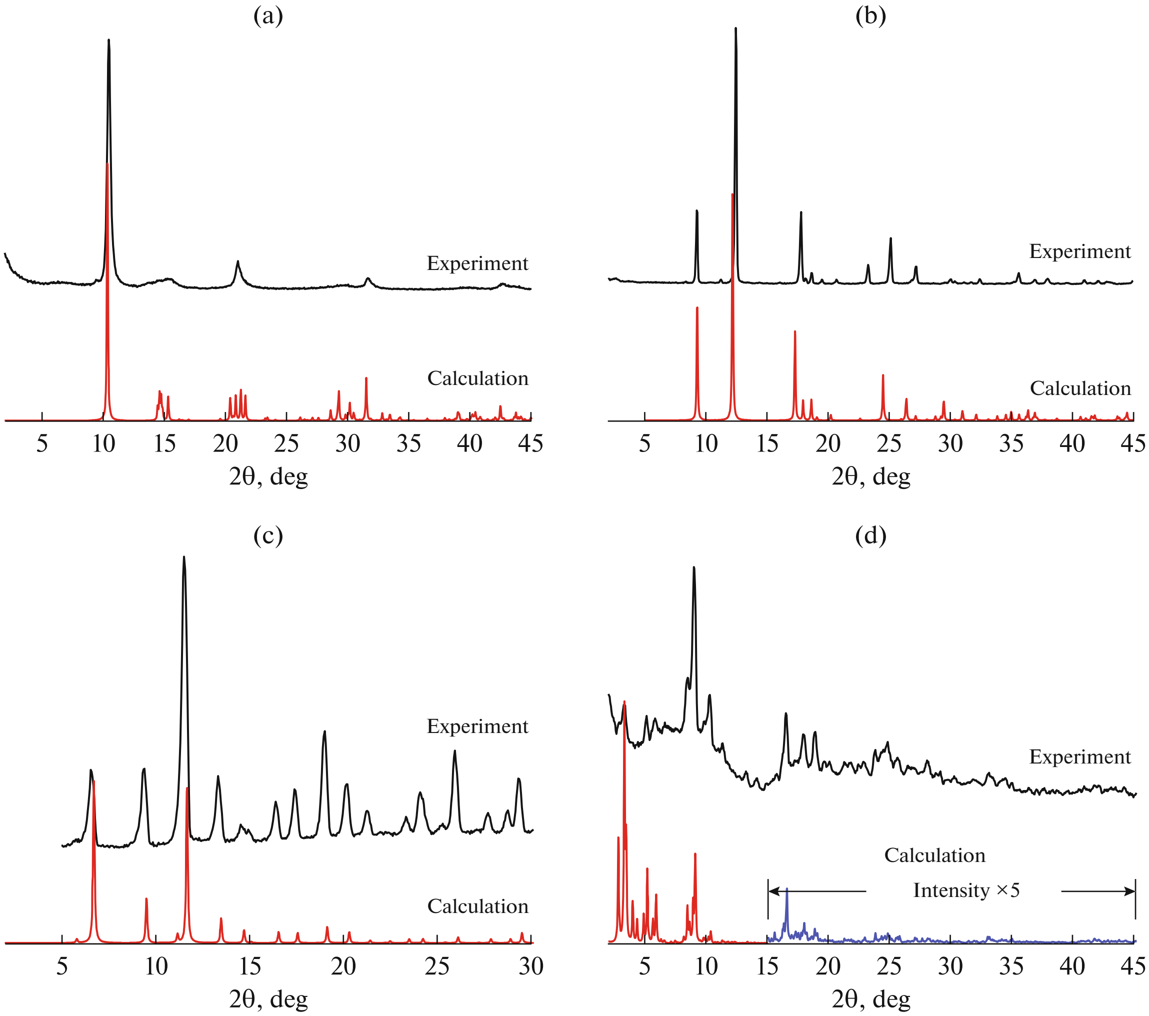


Fig. 1. Experimental and theoretical XRD patterns for compounds (a) **I**, (b) **II**, (c) **III**, and (d) **IV**. The theoretical XRD patterns were calculated for the structures with the parameters indicated in text.

determined by the Saito–Foley method [32] noticeably exceeds the pore size determined from the crystallographic data (for PCP **II**, cf. modification with the space group *Imcm*). In the cases of PCPs **III** and **IV**, on the contrary, the size is smaller (Fig. 3, Table 1). One of the reasons of the difference of the micropore sizes determined from the nitrogen adsorption data and XRD results can be an inaccuracy related to the use of the function parametrized not for PCP (function for nitrogen adsorption on zeolite was used [33]). At the same time, the application of the same approach in the case of the pivalate PCP gave the pore size close to that determined from the structural data [34]. Thus, the differences in the case of PCPs **I** and **II** is caused, most likely, by disordering of their crystalline lattices related to "breathing" rather than to the restricted applicability of the function describing nitrogen adsorption. In the case of PCP **III**, the distribution reflects the presence of "windows" and "cavities" (bimodality of the pore diameter distribution for PCP **III** agrees with that described in [30]). In the case of PCP **IV**, the maximum on the pore diameter distribution curve is weakly pronounced, and it is most likely that the inaccuracy of pore size determination is high. It seems more correct to use the pore diameters calculated from the crystallographic data for the solvated crystals (corresponding to the experimental XRD patterns) for comparing the pore sizes of the PCP and molecules of separated amines, because the amines are adsorbed from solutions and the nitrogen adsorption data show the structures of the thoroughly desolved samples. As mentioned above, the desolvation of PCP **II** leads to a substantial change in its structure.

Thus, according to the estimations presented above, the pore size in PCP **I** is comparable with the size of the studied amine molecules (not lower than 3.9 × 7.7 Å, Table 2) but, as will be shown below, such pores are inaccessible for the studied substrates or the energy barrier of pore filling with these substrates is

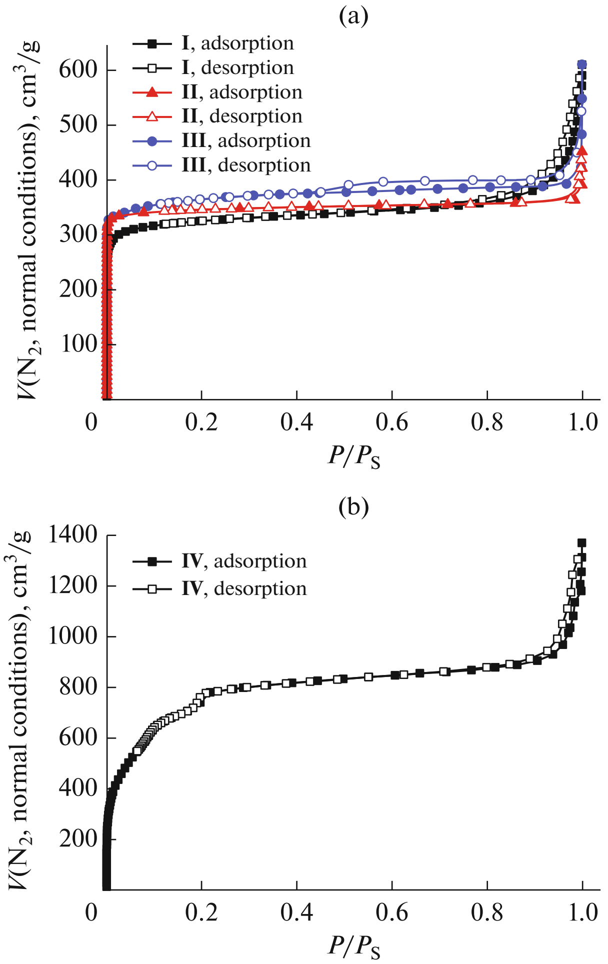


Fig. 2. Nitrogen adsorption isotherms of PCP (a) **I**–**III** and (b) **IV**.

high [35]. The pores in PCP **II** are inaccessible for the studied amines if PCP **II** is not transformed into the conformation with “open” pores during sorption (similarly to the situation described in [29]). At the same time, the pores in PCP **III** and **IV** are potentially accessible for the amines.

An MTBE–*n*-hexane mixture, the choice of which is related to the desire of minimizing the possibility of forming hydrogen bonds of the solvent with PCP and coordinating the solvent to the metal ions in the PCP (especially in PCP **III**), was used in this work for the elution of the amines, which is important for the minimization of the competition of the solvent for the adsorption sites in the PCP. Methyl *tert*-butyl ether was added to *n*-hexane to increase the polarity of the eluent and solubility of the nitroanilines in it. The probability of amine protonation is very low in the chosen mixture of solvents, which is significant for the correct calculation of the measure of hydrophobicity log(*P*) (Table 2).

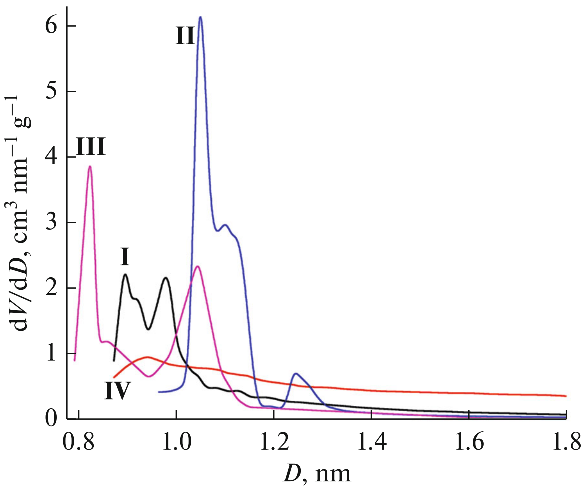


Fig. 3. Micropore diameter distribution for PCP **I**–**IV** calculated from the adsorption isotherms by the Saito–Foley model.

In the experiment on the separation of *m*-nitroaniline **2** and *p*-nitroaniline **3** on the column packed with PCP **I**, amine **3** is eluted first, and its elution from the column starts in approximately 60 min after the experiment onset and finishes in 90 min (hereinafter, the times are indicated from the experiment onset with the accuracy to ±5 min). Isomer **2** begins to elute at the 110th min and is completely eluted at the ~170th min. In a similar experiment using the column with PCP **IV**, the same amines pass the column within ~180 min, and this time is ~60 min in the case of the column with PCP **III**, which is comparable with the time of passing through the column packed with PCP **I**. However, in the case of the columns packed with PCPs **III** or **IV**, no separation of amines **2** and **3** was achieved. In the case of PCP **II**, the amines passed through the column within ~90 min and no separation was observed. The different elution times of the amines from the columns with various PCP are primarily related, most likely, to different permeabilities of the supports (the ability of the liquid to pass through the solid phase particles) but

Table 1. Characteristics of the porous structures of the PCP according to the nitrogen adsorption data

PCP*	S_{BET}, m^2/g	V_{pore}, cm^3/g**	V_{micro}, cm^3/g***	D_{pore}(Saito–Foley), Å****
I	1290	0.645	0.498	9.0
II	1430	0.560	0.535	10.5
III	1435	0.605	0.533	8.2
IV	3160	1.464	0.710	9.5

* The samples were desolvated prior to measurements. ** Gurvich pore volume at $P/P_S = 0.95$. *** Dubinin–Radushkevich micropore volume. **** The values of the first maximum of the pore diameter distribution are presented.

Table 2. Selected physical properties of isomeric amines: nitroanilines and fluoronitroanilines

Name	Size of molecules, Å^3	Polarity, Db	log(P)
2-Amino-1-nitrobenzene (**1**)	7.7 × 8.7 × 3.9	4.14	1.83 ± 0.26
3- Amino-1-nitrobenzene (**2**)	7.9 × 8.6 × 3.9	5.2	1.37 ± 0.24
4-Amino-1-nitrobenzene (**3**)	6.8 × 9.5 × 3.9	6.1	1.39 ± 0.24
2-Amino-3-fluoro-1-nitrobenzene (**4**)	8.8 × 8.2 × 4.2	4.23	2.07 ± 0.37
2-Amino-4-fluoro-1-nitrobenzene (**5**)	7.7 × 9.2 × 3.9	2.96	2.08 ± 0.37
2-Amino-5-fluoro-1-nitrobenzene (**6**)	7.7 × 8.7 × 3.9	4.21	1.94 ± 0.36

Table 3. Results of the separation of substituted nitroanilines on PCP **I**

Elution of amine from column		t_{in}(1st), min	t_{fin}(1st), min	t_{in}(2nd), min	t_{fin}(2nd), min	α*	Order of elution on column with silica gel
1st	2nd						
3	**2**	60	90	110	170	1.8	Inverse
5	**1**	360	1080	1080	1440	3	Coincides
6	**1**	360	1440	720		2	Inverse
5	**4**	120	330	270		2.3	Inverse
6	**4**	360	1440	360		1	Coincides

* $\alpha = t_{in}(2nd)/t_{in}(1st)$.

also can be caused by the difference in their sorption ability to the amines. At the same time, taking into account close values of the elution of the amines in the case of the columns with PCPs **I** and **IV**, we may conclude that the low separation efficiency in the case of PCP **IV** is not related to the difference in the permeability of the PCP layer.

It should be taken into account that the permeability of the PCP can change depending on time because of particle compacting and a change in their morphology under the action of the solvent. To exclude the influence of these factors, we estimated the quantitative characteristics of the efficiency of amine separation by the separation factor α, which was determined as the ratio of the times of the elution onset of the corresponding amines [36] (hereinafter, α was calculated as the ratio of the longer to shorter time for convenience). This approach is used for the characterization of the efficiency of substance separation and to exclude the effect of occasional factors [37]. For the separation of amines **2** and **3** on the column packed with PCP **I**, α is 1.8.

Unlike the column packed with PCP **I**, when amines **2** and **3** are separated on the column with silica gel, amine **2** is eluted first (in ~20 min) and its elution finishes at the 50th min. The elution of **3** begins at the 70th min and finishes at the 80th min. Thus, the order of elution of the amines in a mixture of **2** and **3** on silica gel is "inverted" compared to the order of elution of these amines on PCP **I**, which can be associated with a substantial difference in hydrophilicity/hydrophobicity of the surfaces of these supports. This difference will be discussed below. The efficiency (criterion α) of the separation of amines **2** and **3** on the column packed with silica gel exceeds a similar parameter for PCP **I** and is equal to 3.5.

Taking into account the low efficiency of the separation of amines **2** and **3** on the columns packed with PCP **II–IV**, we carried out experiments on the separation of the fluorine-containing amines only on the columns packed with PCP **I** and with silica gel for comparison. The results of the study are presented in Table 3. A mixture of amines **1** and **5** was separated with the highest efficiency (α = 3). At the same time, a mixture of amines **4** and **6** was not separated. In the case of the separation of amine pairs **2**/**3**, **1**/**6**, and **4**/**5**, the order of elution of these substances on the column with silica gel differs from the observed order of elution on PCP **I**. The change in the order of elution of the amines on the column with PCP compared to silica gel can be explained by the difference in the surface nature. Thus, it is important that the conclusions about the dependence of the efficiency of amine separation on the surface nature are valid only for the PCP with a similar composition and a close chemical structure of the surface.

Since the best result was achieved for a mixture of amines **1** and **5**, we studied the adsorption of these substances on the PCP in an *n*-hexane–MTBE mixture. The PCP samples were not preliminarily desolvated for the best correspondence to the chromatographic separation conditions. The sorption capacity of PCP **I** toward compound **1** exceeds the capacity toward compound **5**, which corresponds to the experimental results on the chromatographic separation of a mixture of the amines: the substance, whose sorption is lower, is first eluted from the column. However, a low sorption capacity of PCP **I** toward these amines should be mentioned, which does not exceed 1×10^{-6} mol per g of the sorbent. It is most likely that the sorption of the amines occurs only on the PCP surface, and the pore filling with the amines if any does not play the key role in chromatographic separation. This conclusion agrees with the results of the separation of amines **1** and **3** on PCP **I**–**IV**: among the studied PCP, compounds **III** and **IV** contain pores, whose size certainly exceeds the pore size of the studied amines (Table 2). However, no separation of the amines occurs on the columns packed with these PCP.

To determine the factors affecting the efficiency of the chromatographic separation of the studied amines on the PCP, we compared the experimental results of the separation of the amines with their physical properties (such as polarity, size of the molecule, and lipophilicity, which characterizes, to some extent, the hydrophobicity of the substance [38]). We failed to find a direct relation between the values of α and the difference or ratio of the dipole moments of the separated amines and the difference in the sizes of the amine molecules. At the same time, a symbate dependence is observed between ln(α) and Δlog(*P*), which is determined as $\log(P)_1 - \log(P)_2$ (Fig. 4). This dependence is consistent with the theoretically expected one: the relationship of the separation factor to the difference in the energies of the interaction of the substance with the support (ΔG) is described by the equation $\Delta\Delta G = -RT\ln(\alpha)$ [39]. Assuming that the equilibrium constant of the substance distribution between the support and eluent K is directly proportional to the constant of its distribution between octanol and water, which serves as a basis for the determination of the lipophilicity parameter $\log P$, and taking into account that $\Delta G = -RT\ln K$, we obtain the equation $\Delta\Delta G = -RT(\ln K_1 - \ln K_2) = -RT(\log P_1 - \log P_2)B$, where B is constant. Then $\ln(\alpha) = B(\log P_1 - \log P_2)$. A similar equation with a correction to the volumes of the mobile and stationary phases was proposed in [40].

Thus, among three studied PCP, the separation of the nitroanilines was observed only on the column packed with PCP **I**. This separation is not related to the pore filling with the amines, which is confirmed by the data on amine adsorption from solutions and is consistent with the results of pore size estimation. PCP **II**–**IV** turned out to be inefficient for the separation of the studied amines when using them as stationary phases for liquid chromatography in spite of pore accessibility in PCP **III** and **IV**. The efficiency of amine separation using PCP **I** is related, most likely, to specific features of the surface of this PCP, which is confirmed by the difference in the order of amine elution during chromatography on the PCP and on silica gel. Among the examined properties of the amines (sizes of molecules, polarity, and lipophilicity), only the last characteristic exerts a noticeable effect on the efficiency of their separation.

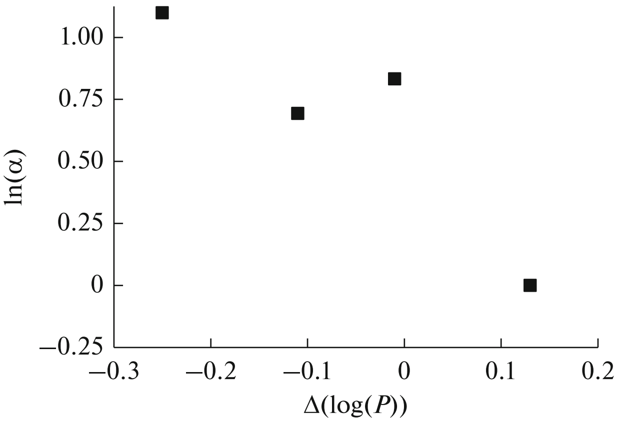


Fig. 4. Dependence of ln(α) on the difference of log(*P*) of the amines.

CONFLICT OF INTEREST

The authors declare that they have no conflicts of interest.

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