

INORGANIC SYNTHESIS AND INDUSTRIAL
INORGANIC CHEMISTRY

Sorption of Aromatic Acids from Aqueous Solutions by Polymer Based on *N*-Vinylpyrrolidone

A. A. Kushnir^a, P. T. Sukhanov^{a*}, A. G. Savvina^a, L. P. Bondareva^a, E. V. Churilina^a,
E. V. Poluzhenkova^a, and G. V. Shatalov^b

^a Voronezh State University of Engineering Technologies, pr. Revolutsii 19, Voronezh, 394036 Russia

*e-mail: pavel.suhanov@mail.ru

^b Voronezh State University, Universitetskaya pl. 1, Voronezh, 394036 Russia

Received March 17, 2016

Abstract—Kinetic and equilibrium characteristics of the sorption of benzoic, salicylic and *ortho*-chlorobenzoic acids by a new cross-linked sorbent based on *N*-vinylpyrrolidone were studied at various pH values of the medium. It was found that the molecular sorption of aromatic carboxylic acids from aqueous solutions occurs in the mixed-diffusion mode and the sorption capacity of the polymer grows with increasing acid-base equilibrium constants of the acids. The advisability of introducing a salting-out agent into sorption systems was confirmed. Effective sorption systems and a method for concentration of aromatic carboxylic acids from aqueous solutions by the new cross-linked sorbent based on *N*-vinylpyrrolidone were suggested.

DOI: 10.1134/S1070427216060070

Aromatic carboxylic acids are widely used in production of food products as conserving agents, as dermatic antiseptic (antimicrobial) and fungicidal (antimycotic) means in medicine, and in syntheses of benzoate plasticizers (glycol, diethylene glycol, and triethylene glycol esters), anthraquinone-oxazol dyes (Vat red), and fragrant substances (salicylic acid esters). However, excess amounts of any additives may lead to allergic reactions and imbalance of active substances in an organism; the sanitary regulations of various countries control the content of aromatic carboxylic acids in food products to below the admissible daily dose [1].

Because aromatic carboxylic acids are contained in food and pharmaceutical products in microscopic concentrations, the sorption is the most needed and effective extraction method.

Of practical interest are polymeric sorbents based on *N*-vinylpyrrolidone (NVP), which are characterized by a high efficiency with respect to organic compounds of various classes [2].

The goal of our study was to determine the fundamental aspects of the extraction of aromatic acids and

to develop a method for their concentration from dilute aqueous media by a new cross-linked polymer based on *N*-vinylpyrrolidone.

EXPERIMENTAL

We used benzoic (BA), salicylic (SA), and *ortho*-chlorobenzoic (CBA) acids purified by recrystallization of commercial preparations and identified by their melting points. Working solutions were prepared by dissolution of precisely weighed portions of the starting substances in distilled water.

The aromatic carboxylic acids were concentrated by the sorbent (synthesized by the procedure described in [2] at the chair of chemistry of micromolecular compounds and colloids of Voronezh State University) produced by radical copolymerization of a functional monomer, *N*-vinylpyrrolidone, and a cross-linking agent, ethylene glycol dimethacrylate (EGDMA), in the presence of a polymerization-initiating agent (azo-bis-butyrac acid dinitrile).

Chlorides and sulfates of sodium, potassium, and ammonium (salting-out agents) were twice recrystallized

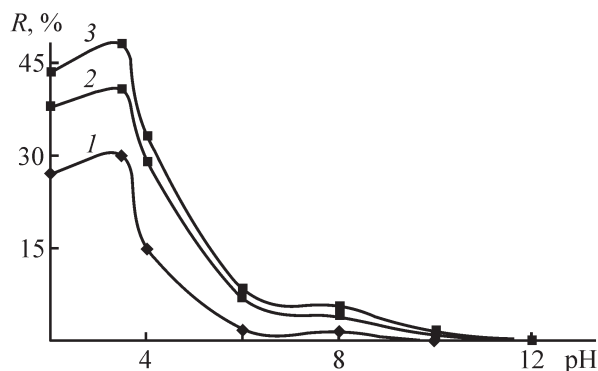


Fig. 1. Dependence of the recovery R of (1) BA, (2) SA, and (3) CBA by the polymeric sorbent based on *N*-vinylpyrrolidone on the pH of the aqueous phase. $C_0 = 0.1 \text{ mg mL}^{-1}$, $V = 10 \text{ mL}$, $m = 0.05 \text{ g}$, $t = 60 \text{ min}$.

from distilled water from preparations of chemically pure grade.

To examine the sorption of aromatic acids in the static mode, weighed portions ($0.050 \pm 0.001 \text{ g}$) of the sorbents were placed in test tubes with ground-in stoppers, 10-cm³ portions of the sorbate solution with increasing concentrations were added, and the mixtures were agitated on a vibration mixer at a constant temperature until a sorption equilibrium was attained [3]. After that the sorbent was separated from the solution by decantation and the concentration of a compound under study in the equilibrium aqueous phase was spectrophotometrically determined. The measurements were made on a Shimadzu UV 1240 spectrophotometer at a wavelength λ (nm) corresponding to the maximum absorption of aromatic acids (BA 272, SA 275, and CBA 290) in quartz cuvettes with a 1-cm-thick absorbing layer. The pH of the medium was controlled potentiometrically.

The recovery R (%) and the sorption a_e (mmol g⁻¹) were calculated by the equations

$$R = 100(c_0 - c)/c_0,$$

$$a_e = [(c_0 - c)V]/m,$$

where c_0 and c are the concentrations of the compound being determined in the starting and equilibrium solutions, respectively (mmol mL⁻¹); V , volume of the aqueous solution (mL); and m , sorbent mass (g).

The concentration factor K was calculated by the formula

$$K = m_{\text{aq}}/m_{\text{org}},$$

where m_{aq} and m_{org} are the masses of the aqueous and organic phases, respectively.

To examine the sorption kinetics, 0.050-g weighed portions of the sorbents were placed in thermostated vessels with ground-in stoppers, 10-mL portions of acid solutions with a certain concentration was added, and the mixtures were mixed on a vibration mixer. The sorption was performed at $22 \pm 1^\circ\text{C}$ and pH ~ 3.0 . After a certain time, the sorbent was separated from the solution by filtration and the concentration of the acids in the equilibrium aqueous phase was spectrophotometrically determined.

The sorption a_t (mmol g⁻¹) at certain instants of time was calculated by the formula

$$a_t = [(c_0 - c_t)V]/m,$$

where c_t is the acid concentration after a certain time (mmol mL⁻¹).

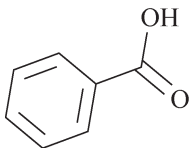
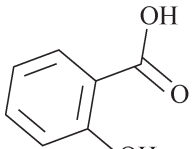
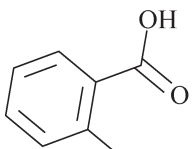
RESULTS AND DISCUSSION

Under the static conditions, the recovery of microcomponents is determined by the distribution coefficients of the sorbate and by the time (rate) at which the sorption equilibrium is attained, with this rate being an important characteristic of any solid-phase concentration process and having a practical and theoretical importance [4]. The practical implementation of these processes assumes that the sorbent can be absorbed during a short time of contact between the substance and the sorbent.

As regards the whole set of kinetic characteristics (shorter time in which the sorption equilibrium is attained and the higher rate of formation of sorbate-sorbent bonds), the optimal sorbent for concentration of organic compounds, determined for the example of sorption of nitrophenol from aqueous media in the static mode, is the sorbent produced by polymerization in a CH₃OH solution at NVP : EGDMA = 1 : 15 in the prepolymerization mixture [2, 5].

The aromatic carboxylic acids chosen for study differ in the hydrophobicity, which is evaluated by Ganja-Leo coefficients logP, acid dissociation constants pKa, and presence of various substituents in the aromatic ring (Table 1). Aromatic carboxylic acids contain simultaneously a polar carbonyl group and a hydrophobic aromatic ring, and, therefore, their sorption efficiency strongly depends on the pH value of an aqueous solution. The acids are extracted in the molecular form: the maximum

Table 1. Ganja–Leo coefficients $\log P$, acid-base equilibrium constants $\text{p}K_a$, recovery R , maximum sorption a_p^{max} , and sorption equilibrium constants k_g of aromatic acids by a polymeric sorbent based on *N*-vinylpyrrolidone

Acid	Structural formula	$\log P^a$ (pH 3)	$\text{p}K_a^a$	$R, ^b \%$	$a_p^{\text{max}}, \text{mmol g}^{-1}$	k_g
Benzoic		1.53	4.20 ± 0.10	32 ± 2	0.129	1.75
Salicylic		1.55	2.97 ± 0.25	41 ± 3	0.174	2.11
<i>ortho</i> -Chlorobenzoic		1.13	2.97 ± 0.25	49 ± 2	0.271	2.07

^a The constants were calculated by software for $\log P$ and $\text{p}K_a$ (© ACD/Inc, Toronto, Canada).

^b $V = 10 \text{ mL}$, $m = 0.05 \text{ g}$, $\text{pH } 3$, $n = 3$, $P = 0.95$.

sorption (Fig. 1) is reached at $\text{pH} \sim 3$, at which the acid group is not dissociated. As the pH value increases from 4 to 10, the number of not dissociated molecules decreases and the recovery of the acids becomes smaller.

According to the kinetic curves in Fig. 2, the sorption a_t (mmol g^{-1}) of BA, SA, and CBA first linearly grows and then gradually increases to reach a nearly constant value. As the initial concentration of the sorbate in solution increases, so does their recovery at a somewhat shorter phase contact duration.

The steep rise in a_t during the initial period of time (up to 8 min) can be attributed to the larger number of free active centers, which gives rise to a substantial concentration gradient between the ions being sorbed in solution and in the sorbent phase [6]. Due to the accumulation of the sorbate (from 8th min until attainment of the sorption equilibrium), the concentration gradient on active centers decreases, and the sorption rate becomes lower. The sorption equilibrium is attained for all the aromatic carboxylic acids in 40–50 min.

It was assumed that the sorption rate is determined at low sorbate concentrations by the diffusion of a component to the sorbent surface. The hypothesis was confirmed by approximation of the experimental kinetic curves plotted in the coordinates

$$\ln(1-F) = f(t),$$

where t is the time of contact between the sorbent and the sorbate solution (min), $F = a_t/a_e$, and a_e is the equilibrium amount of the sorbent (mmol g^{-1}) [7].

Dependences of this kind are characteristic of outer-diffusion processes. Their linear run with a high

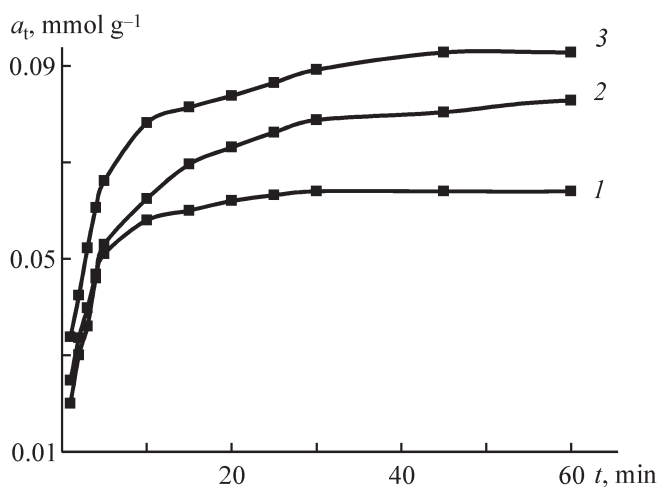


Fig. 2. Kinetic curves for sorption of aromatic carboxylic acids (1) BA, (2) SA, and (3) CBA by the polymeric sorbent based on *N*-vinylpyrrolidone. $\text{pH} \sim 3$, $c_0 = 0.1 \text{ mg mL}^{-1}$, $V = 10 \text{ mL}$, $m = 0.05$. (t) Time; the same for Figs. 3 and 4.

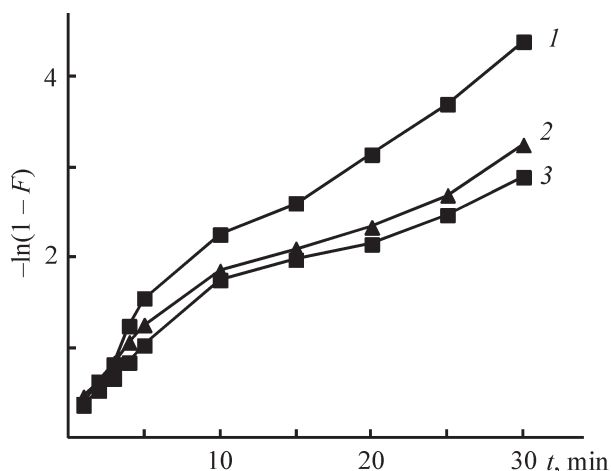


Fig. 3. Kinetic curves for sorption at of aromatic carboxylic acids (1) BA, (2) SA, and (3) CBA, plotted in the characteristic coordinates of the outer-diffusion limitation $-\ln(1-F)-t$.

correlation coefficient was found in the initial portion during the first 10 min of the process (Table 2), with the linearity disrupted during its further development. Consequently, the outer-diffusion sorption kinetics of aromatic carboxylic acids occurs at low degrees of filling of the polymeric sorbent.

To find the rate-determining stage of the process upon an increase in the degree of filling of the polymeric sorbents, we approximated the kinetic dependences in the coordinates suggested by Weber and Morris. If the function of the specific amount of sorbed components, a_t (mmol g^{-1}), on time t (min) is linear in the coordinates

$$a_t = k_p t^{0.5},$$

where k_p is the rate constant of the inner diffusion ($\text{mmol g}^{-1} \text{min}^{-0.5}$), then the process is diffusion-controlled [8]. The kinetic curves in Fig. 4 do not originate from the zero of the coordinate system and have two

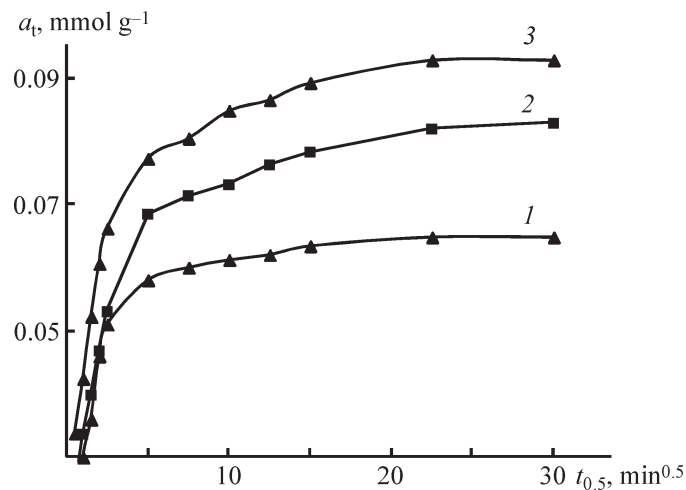


Fig. 4. Kinetic curves for sorption at of aromatic carboxylic acids (1) BA, (2) SA, and (3) CBA, plotted in the characteristic coordinates of the inner-diffusion limitation $a_t - t_{0.5}$.

portions: the first up to 8th min is nearly linear, but its correlation coefficient does not exceed 0.9; and the second, extending until equilibrium is attained, is linear with a large correlation coefficient (Table 2).

Thus, the results we obtained suggest that the sorption process occurs in the mixed-diffusion mode. At the beginning of the process, when there are free active centers on the surface of the polymeric sorbent, the absorption occurs with limited sorbate diffusion at the surface. Further, the influence of the outer-diffusion factor decreases, and that of the inner-diffusion factor grows, and then the sorption process passes to the mode in which the transfer in the polymer phase is limited.

At the chosen pH values an equilibrium attainment time, sorption isotherms (Fig. 5) of aromatic carboxylic acids were obtained, which belong according to the IUPAC classification to type-1 isotherms of localized reversible adsorption on active energetically uniform centers [9]. The surface of the sorbents is saturated by

Table 2. Kinetic equations for sorption of aromatic acids, plotted in the characteristic coordinates $-\ln(1-F) = f(t)$, in portion 1 (up to 5th min of the process) and $a_t = f(t_{0.5})$ in portion 2 (after 10 min of the process)

Acid	Portion 1		Portion 2	
	kinetic equation $\ln(1-F) = f(t)$	r^2	kinetic equation $a_t = f(t_{0.5})$	r^2
BA	$y = 0.297x + 0.025$	0.983	$y = 5.1 \times 10^{-5}x + 5.6 \times 10^{-3}$	0.987
SA	$y = 0.164x + 0.184$	0.996	$y = 5.7 \times 10^{-5}x + 6.7 \times 10^{-3}$	0.962
CBA	$y = 0.204x + 0.227$	0.996	$y = 8.4 \times 10^{-5}x + 7.5 \times 10^{-3}$	0.979

Table 3. Recovery of aromatic acids from 0.5 M aqueous solutions of salts by the polymeric sorbent based on *N*-vinylpyrrolidone ($V = 10$ mL, $m = 0.05$ g, pH 3)

Acid	Recovery R , %						
	without salting-out agent	in the presence of a salting-out agent					
		$(\text{NH}_4)_2\text{SO}_4$	NH_4Cl	Na_2SO_4	K_2SO_4	KCl	NaCl
BA	32	61	54	45	42	35	33
SA	41	69	59	53	48	43	42
CBA	49	78	68	59	55	53	50

molecules of aromatic carboxylic acids at rather low equilibrium concentrations, which characterizes the high affinity of sorbates for the polymers under study. The linear portions of the isotherms decrease with increasing constants of the acid-base equilibrium of the sorbates, which confirms the molecular nature of the sorption interaction in the systems under study.

The experimental sorption isotherms were processed by the Langmuir and Freundlich sorption equations [10]. The largest correlation coefficients ($r^2 = 0.990$ – 0.999) were found by plotting the sorption isotherm in the coordinates of the Langmuir equation; these coefficients can be used for calculating the maximum sorption a_p^{\max} and the sorption-equilibrium coefficients k_g (Table 1).

It was found that the amount of an absorbed acid grows as the constants of the acid-base equilibrium decrease. The affinity of the aromatic carboxylic acids under study for the polymeric sorbent can be arranged in order $\text{BA} < \text{SA} < \text{CBA}$.

The sorption of the aromatic carboxylic acids under study is affected not only by $\text{p}K_a$ values (Table 1), but also by the Ganja–Leo coefficient $\log P$. If the compounds being distributed have comparable $\text{p}K_a$ values (SA and CBA), then the more hydrophobic CBA is better sorbed. Studies have demonstrated the molecular (extraction) sorption mechanism of the acids under study [11, 12], which suggested that the recovery grows in the presence of salting-out agents. With increasing degree of hydration of salt ions, their interaction with water is enhanced, with the amount of free water decreasing and, accordingly, the degree of sorbate hydration becoming smaller. Various salts frequently used in practice were chosen as salting-out agents (Table 3). It was found that the salts can be arranged in order of decreasing efficiency of the salting-out effect as follows: $(\text{NH}_4)_2\text{SO}_4 > \text{NH}_4\text{Cl} > \text{Na}_2\text{SO}_4 > \text{K}_2\text{SO}_4 > \text{NaCl} > \text{KCl}$.

The salting-out efficiency coincides with the ordering-disordering effect of the corresponding ions on the structure of water [13]. For example, the difference in the degrees of recovery of ions having the same charge is due to the dissimilar extents of the hydration. The more strongly an ion is hydrated, the weaker its attraction to the oppositely charged surface and, accordingly, its hydration requires a larger amount of water, which leads to a lower hydration of the sorbate.

In systems with ammonium sulfate, the recovery increases by nearly 30%, compared with the sorption from an aqueous solution, similarly to the *N*-vinylpyrrolidone-based polymer studied in sorption of nitrophenols from aqueous media [14].

Based on the results of the study in which the time of attainment of the sorption equilibrium and the maximum

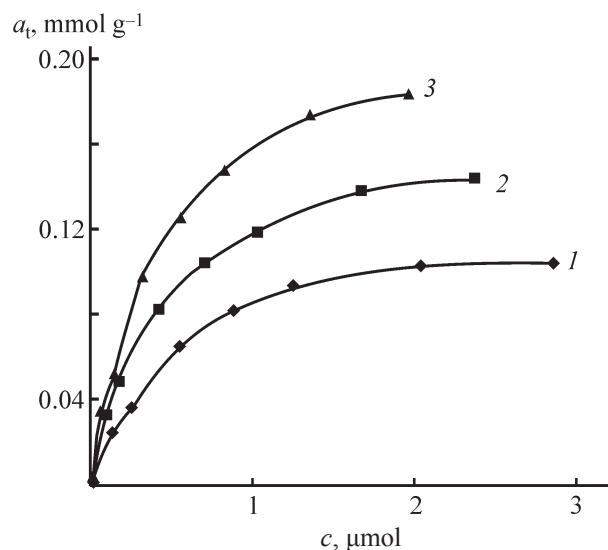
**Fig. 5.** Sorption isotherms as of aromatic carboxylic acids (1) BA, (2) SA, and (3) CBA by the polymeric sorbent based on *N*-vinylpyrrolidone from an aqueous solution at 298 K. $T = 60$ min, $V = 10$ mL, $m = 0.05$ g, pH ~ 3 .

Table 4. Recovery and concentration coefficients of aromatic acids by the polymeric sorbent based on *N*-vinylpyrrolidone from a 0.5 M solution of ammonium sulfate ($m = 0.1$ g, $V = 10$ mL, pH 3)

Acid	R , %	K
BA	97	103
SA	99	100
CBA	99	100

recovery at the optimal pH value of the medium were determined and the necessity for introduction of a salting-out agent was confirmed, we suggest a method for concentration of aromatic carboxylic acids from dilute aqueous solutions. In this method, a sample taken from a solution of an aromatic carboxylic acid is acidified to pH 3 with an HCl solution, crystalline ammonium sulfate is added until a solution with concentration of 0.5 mol dm^{-3} is obtained, a polymeric sorbent is introduced at a 100 : 1 ratio between the water-salt solution and the sorbent, the mixture is agitated on a vibration mixer for 50 min, and the polymer with the sorbate are separated from the aqueous phase. Irrespective of the nature of an acid, a 100-fold concentration is provided at a nearly complete extraction (97–99%) from their dilute aqueous solutions (Table 4).

CONCLUSIONS

(1) The molecular (extraction) mechanism was identified on the basis of kinetic sorption curves and sorption isotherms and it was found that the sorption process occurs in the mixed diffusion mode.

(2) It is recommended to use a cross-linked sorbent based on *N*-vinylpyrrolidone to perform a 100-fold

concentration of aromatic carboxylic acids from dilute aqueous solutions. A nearly full extraction (97–99%) is reacted at pH 3 in the presence of a salting-out agent (ammonium sulfate).

REFERENCES

1. *Pishchevye dobavki: Spravochnik* (Food Additives: Reference Book), Buldakov, A.S., Ed., Moscow: DeLi print, 2003.
2. Churilina, E.V., Kushnir, A.A., Sukhanov, P.T., et al., *J. Anal. Chem.*, 2015, vol. 70, no. 2, pp. 130–135.
3. Larin, A.V., Svitova, T.F., Frolova, E.A., et al., *Kolloid. Zh.*, 1993, vol 55, no. 3, pp. 109–113.
4. Neudachina, L.K., Petrova, Yu.S., Zasukhin, A.S., et al., *Analitika Kontrol'*, 2011, vol. 15, no. 1, pp. 87–95.
5. Sukhanov, P.T., Kushnir, A.A., Bondareva, L.P., et al., *Sorbtsionnye Khromatogr. Protsessy*, 2015, vol. 15, no. 2, pp. 224–232.
6. Neudachina, L.K., Golub, A.Ya., and Kholmogorova, A.S., *Russ. J. Appl. Chem.*, 2014, vol. 87, no. 7, pp. 923–929.
7. Wang, S., and Li H., *Dyes Pigment.*, 2007, vol. 72, no. 3, pp. 308–314.
8. Li, N. and Ba, R., *Sep. Purif. Technol.*, 2005, vol. 42, no. 3, pp. 237–247.
9. Karnaukhov, A.P., *Adsorbtsiya. Tekstura dispersnykh i poristykh materialov* (Adsorption. Texture of Dispersed and Porous Materials), Novosibirsk: Nauka, 1999.
10. Frolov, Yu.G., *Poverkhnostnye yavleniya i dispersnye* (Surface and Dispersion Phenomena), Moscow: Khimiya, 1982.
11. Liu, Y., *J. Chem. Eng.*, 2009, vol. 54, pp. 1981–1985.
12. Schumak, L. and Chow, A., *Talanta*, 1987, vol. 34, no. 11, pp. 957–962.
13. Karyakin, A.V. and Kriventsova, G.A., *Sostoyanie vody v organicheskikh i neorganicheskikh soedineniyakh* (State of Water in Organic and Inorganic Compounds), Moscow: Nauka, 1973.
14. Churilina, E.V., Kushnir, A.A., Sukhanov, P.T., et al., *Russ. J. Gen. Chem.*, 2013, vol. 83, no. 11, pp. 2032–2036.