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RESEARCH ARTICLE

Sorption of picolinic acid by Cu(II)-containing sulfocationite KU-2-8

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Abstract

Objectives. To study the equilibrium distribution of components between KU-2-8 sulfocationite and an aqueous solution containing picolinic acid and Cu(II); to show the possibility of immobilization of cations of picolinic acid and Cu^{2+} in sulfonic cation exchanger KU-2-8; to calculate the component compositions of the equilibrium solution, in order to obtain the required ionic composition of the KU-2-8 sulfonic cation exchanger according to the selectivity coefficients of binary ion exchange, and the constants of formation of such complexes in water.

Methods. The concentrations of the individual components in multicomponent solutions were calculated using the HySS 2009 program (Hyperquad Simulaton and Speciation). The calculation of the equilibrium ionic compositions of KU-2-8 sulfocationite was performed using the selectivity coefficients of binary ion exchanges and the formation constants of complexes of picolinic acid with Cu^{2+} and H^+ cations. Experimental study of the equilibrium distribution of components between aqueous solutions of picolinic acid, copper nitrate, and KU-2-8 sulfocationite was carried out by means of the dynamic method at a temperature of 298 K. Fourier-transform infrared spectroscopy and electron paramagnetic resonance spectroscopy were used, in order to determine the ionic forms of the components contained in the sulfocationite.

Results. It was shown that the equilibrium solution contains H^+ protons, Cu^{2+} cations, LH picolinic acid molecules, protonated picolinic acid cations $[H_2L]^+$, deprotonated picolinic acid anions L^-, Cu^{2+} complexes with the deprotonated picolinic acid anion $[CuL]^+$, and Cu^{2+} complexes with two anions of deprotonated picolinic acid $[CuL_2]$. The concentration of H^+, Cu^{2+}, and $[H_2L]^+$ cations in the solution significantly exceeds the concentration of other components at pH values from 0 to 0.5. The content of $[CuL]^+$ cations and neutral complexes $[CuL_2]$ increases significantly in the solution, while the $[H_2L]^+$ cations disappear at pH greater than 1. It was experimentally established that the concentrations of picolinic acid and copper in the polymer phase are many times higher than the concentrations of these components in an aqueous solution. The partition coefficients are about 24 and 210 for picolinic acid and Cu(II), respectively. The calculated dependencies of the concentrations of Cu^{2+}, $[H_2L]^+$, H^+, $[CuL]^+$ cations in the polymer *vs* pH of an equilibrium solution containing picolinic acid were obtained. The experimental data on the concentrations of all cations in the ion exchanger is in the intervals of the calculated compositions within the limits of measurement errors.

Conclusions. KU-2-8 sulfocationite is proposed as a container for obtaining drugs based on picolinic acid and Cu^{2+} cations. It was shown that the selectivity coefficients of binary ion exchanges and the formation constants of $[H_2L]^+$, $[CuL]^+$ complexes can be used to precalculate the ionic compositions of the equilibrium solution, in order to obtain the required compositions of the sulfocationite.

Keywords

KU-2-8 sulfocationite, picolinic acid, copper(II) cations, sorption

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НАУЧНАЯ СТАТЬЯ

Сорбция пиколиновой кислоты Cu(II)-содержащим сульфокатионитом КУ-2-8

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Аннотация

Цели. Изучить равновесное распределение компонентов между сульфокатионитом КУ-2-8 и водным раствором, содержащим пиколиновую кислоту и Cu(II); показать возможность иммобилизации катионов пиколиновой кислоты и Cu^{2+} в сульфокатионите КУ-2-8. Выполнить предрасчет компонентного состава равновесного раствора для получения необходимого ионного состава сульфокатионита КУ-2-8 по коэффициентам селективности бинарных ионных обменов и константам образования комплексов в воде.

Методы. Концентрации индивидуальных компонентов в многокомпонентных растворах рассчитывали с помощью программы HySS 2009 (Hyperquad Simulaton and Speciation). Расчет равновесных ионных составов сульфокатионита КУ-2-8 выполнен по коэффициентам селективности бинарных ионных обменов и константам образования комплексов пиколиновой кислоты с катионами Cu^{2+} и H^+. Экспериментальное исследование равновесного распределения компонентов между водными растворами пиколиновой кислоты, нитрата меди и сульфокатионитом КУ-2-8 проведено динамическим методом при температуре 298 К. Для определения ионных форм компонентов, содержащихся в сульфокатионите, использованы инфракрасная спектроскопия с преобразованием Фурье и спектроскопия электронного парамагнитного резонанса.

Результаты. Показано, что в равновесном растворе содержатся протоны H^+, катионы Cu^{2+}, молекулы пиколиновой кислоты LH, катионы протонированной пиколиновой кислоты $[H_2L]^+$, анионы депротонированной пиколиновой кислоты L^-, комплексы Cu^{2+} с анионом депротонированной пиколиновой кислоты $[CuL]^+$, комплексы Cu^{2+} с двумя анионами депротонированной пиколиновой кислоты $[CuL_2]$. При значениях pH от 0 до 0.5 в растворе концентрация катионов H^+, Cu^{2+}, $[H_2L]^+$ существенно превышает концентрацию других компонентов, при pH больше 1 в растворе значительно увеличивается содержание катионов $[CuL]^+$, нейтральных комплексов $[CuL_2]$ и практически исчезают катионы $[H_2L]^+$. Экспериментально установлено, что концентрация пиколиновой кислоты и меди в полимерной фазе во много раз превышает концентрацию этих компонентов в водном растворе. Коэффициенты распределения составляют примерно 24 и 210 для пиколиновой кислоты и Cu(II) соответственно. Получены расчетные зависимости концентрации катионов Cu^{2+}, $[H_2L]^+$, H^+, $[CuL]^+$ в полимере от pH равновесного раствора, содержащего пиколиновую кислоту. Экспериментальные данные о концентрациях всех катионов в ионите в пределах ошибок измерений попадают в интервалы расчетных составов.

Выводы. Сульфокатионит КУ-2-8 предложен в качестве контейнера для получения лекарственных препаратов на основе пиколиновой кислоты и катионов Cu^{2+}. По коэффициентам селективности бинарных ионных обменов и константам образования комплексов $[H_2L]^+$, $[CuL]^+$ выполнен предрасчет компонентного состава равновесного раствора для получения необходимого ионного состава сульфокатионита КУ-2-8.

Ключевые слова

сульфокатионит КУ-2-8, пиколиновая кислота, катионы меди, сорбция

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INTRODUCTION

Pyridine carboxylic acids are an object of interest to researchers. Picolinic acid (2-pyridinecarboxylic acid) is known for its antibacterial activity against *S. aureus*, *S. epidermidis*, *E. coli* [1]. Fusaric acid, a picolinic acid derivative, possesses antibacterial, insecticidal, bactericidal activity [2], while picolinic acid amides possess anti-inflammatory and analgesic activity [3]. Copper is widely used in medicine as an anti-inflammatory, styptic, antibacterial and antipyretic agent [4, 5]. In pharmacology, Ehrlich's idea of the feasibility of targeted drug delivery to the focus of disease is becoming increasingly relevant [6]. The use of nanocontainers [7] helps to achieve the desired pharmacokinetics, opening up significant opportunities for the preservation and storage of dosage forms. They also enable the vector delivery of drug substance to the focus of the disease. Studies on the creation of polymer and biocomposite matrices as carriers of target pharmaceutical substances [8] and nanocontainers on matrices of mesh polymers are of topical relevance [9].

In the food industry and medicine, the deep desalination of water, as well as purification of vitamins and pharmaceuticals, is achieved with the help of sulfonated copolymer of styrene with divinylbenzene (industrial KU-2-8 cationite or Dowex 50) [10]. A known property is its complementarity to pyridinecarboxylic acids, possessing the highest capacity among other sulfocationites [11]. It was shown [11] that the elementary link of sulfonated styrene copolymer with divinylbenzene is a nanocarrier for pyridinecarboxylic acid (Fig. 1).

We previously studied the sorption of nicotinic and isonicotinic acids by Dowex-50 sulphocationite in Ni(II)- and Cu(II)-form and Ag-containing KU-2-4 sulphocationite [12, 13].

The objectives of this study were:

- To study the equilibrium distribution of components between KU-2-8 sulphocationite and aqueous solution containing picolinic acid and Cu(II); and to show the possibility of immobilization of picolinic acid and Cu^{2+} cations in KU-2-8 sulphocationite;
- To precalculate the component composition of the equilibrium solution, in order to obtain the required ionic composition of KU-2-8 sulphocationite according to the selectivity coefficients of binary ionic exchanges and constants of complex formation in water.

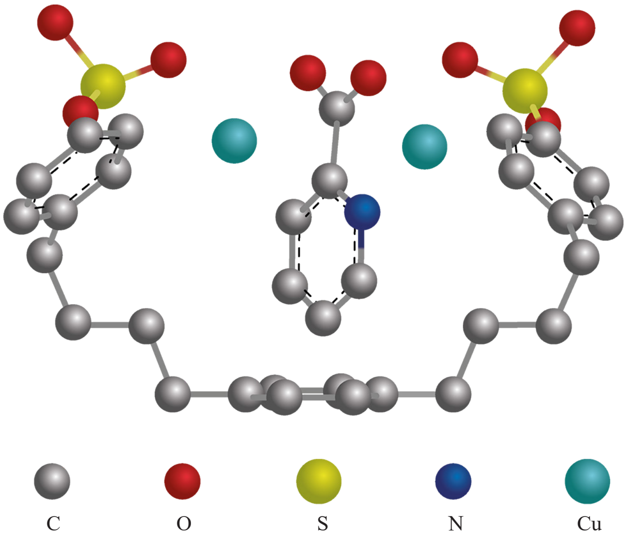

Fig. 1. Structure of a nanocontainer (an elementary unit of sulfonated copolymer of styrene with divinylbenzene) containing pyridinecarboxylic acid [11], minimized in terms of internal energy using the MOPAC 2016 program[1]

MATERIALS AND METHODS

Strong-acid KU-2-8 cationite (sulfonated copolymer of styrene with 8% divinylbenzene) has a gel structure, and contains SO_3H-groups as ionogenic groups. The total ion exchange capacity is 5.0 mEq per 1 g of H-form of the dry polymer (2.0 mol per 1 L of native volume of the swollen ion exchanger phase). Picolinic (2-pyridinecarboxylic) acid (*Kiev plant RIAP*, Ukraine) contained at least 98.0% of the basic substance. The electrolyte solutions were prepared from $Cu(NO_3)_2$ (*Ural Plant of Chemical Reagents*, Russia), HNO_3, $NaNO_3$ (*Mikhailovsky Plant of Chemical Reagents*, Russia), chemically pure grade.

The equilibrium distribution of components between aqueous solutions of picolinic acid, copper nitrate and KU-2-8 sulfocationite was studied by means of the dynamic method at 298 K. The working interval of pH of equilibrium solutions was chosen in the range of 2.0–2.5. This was based on the content of components in the solution, and their ability to participate in the cation exchange reaction. The multicomponent aqueous solutions were passed through an ion-exchange column filled with the Cu^{2+}-form of polymer (5 mL of swollen ionite) until equilibrium was established (until the compositions and pH of the initial solution and filtrate coincided). The equimolar concentrations of picolinic acid and

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[1] MOPAC (Molecular Orbital PACkage) is the semi-empirical quantum chemistry program developed by James J. P. Stewart, Stewart Computational Chemistry, Colorado Springs, Colorado, USA, http://openmopac.net/. Accessed December 12, 2023.

copper nitrate in the solutions were maintained near 0.005 mol/L (at picolinic acid concentrations above 0.01 mol/L, a precipitate of complexes containing Cu(II) and picolinic acid forms in the solution). After reaching the equilibrium state, desorption of picolinic acid and copper was carried out using a 0.1 M $NaNO_3$ solution. The concentration of picolinic acid in the solutions was measured using a spectrophotometer SF-46 (*LOMO*, Russia) at $\lambda = 262.7$ nm and pH = 6.86.

The total copper concentration in the multicomponent solutions $(\sum C_{\mathrm{Cu}})$ was determined by means of complexometric titration. The concentrations of the individual components C_i in solutions were calculated using HySS 2009 software[2]. The concentration of components in the polymer $(\overline{C}_i)$ was calculated in moles per liter of the native volume of the swollen ionite phase. Infrared (IR) spectra were obtained using an Infralum FT-801 FTIR spectrometer (*SIMEX*, Russia) in KBr tablets. The electron paramagnetic resonance spectra were recorded on a Bruker EMX micro 6/1 electron spin resonance (ESR) spectrometer (*Bruker EMX*, Germany) at room temperature (20°C). The number of paramagnetic centers was calculated by comparison with a standard sample (Mn^{2+} in MgO). The spectra were processed using the WinEPR software package[3].

RESULTS AND DISCUSSION

The experimental data thus obtained is presented in Table 1.

Table 1. Equilibrium compositions of KU-2-8 sulfocationite and aqueous solutions containing $Cu(NO_3)_2$ and picolinic acid at 298 K

Solution			Sulfocationite	
pH	$\sum C_{\mathrm{Cu}}$	$\sum C_{\mathrm{HL}}$	$\sum \overline{C}_{\mathrm{Cu}}$	$\sum \overline{C}_{\mathrm{HL}}$
	mol/L			
2.00	0.005	0.0053	1.04	0.144
2.13	0.005	0.0052	1.04	0.104
2.20	0.005	0.0053	1.06	0.144
2.28	0.005	0.0053	1.05	0.097
2.39	0.005	0.0054	1.05	0.145

Table 1 shows that the concentration of picolinic acid and Cu(II) in the polymer phase is many times higher than that of the same components in aqueous solution. The distribution ratios $(\overline{C}_i / C_i)$ are approximately 24 and 210 for picolinic acid and Cu(II), respectively.

Let us consider the reasons of occurrence of high distribution ratios. The following reactions take place in the solution being studied:

$$L^- + H^+ = HL, \tag{1}$$

$$HL + H^+ = [H_2L]^+, \tag{2}$$

$$Cu^{2+} + L^- = [CuL]^+, \tag{3}$$

$$[CuL]^+ + L^- = [CuL_2]. \tag{4}$$

These reactions can be characterized by the constants of complex formation as presented in Table 2.

Table 2. Stability constants β[4]

Substance	lgβ
HL (picolinic acid)	5.184
$[H_2L]^+$	6.066
$[CuL]^+$	7.9
$[CuL_2]$	14.75

The equilibrium solution contains protons H^+, cations Cu^{2+}, molecules of picolinic acid LH, cations of protonated picolinic acid $[H_2L]^+$, anions of deprotonated picolinic acid L^-, Cu^{2+} complexes with an anion of deprotonated picolinic acid $[CuL]^+$, and Cu^{2+}complexes with two anions of deprotonated picolinic acid $[CuL_2]$. Figure 2 shows the equilibrium ratio of components in solution as calculated using the HySS 2009 software. At pH values from 0 to 0.5 in the solution the concentration of cations H^+, Cu^{2+}, $[H_2L]^+$ significantly exceeds the concentration of other components. The concentration of H^+ exceeds the concentration of Cu^{2+}, $[H_2L]^+$ by more than 2 orders of magnitude. At a pH level from 0.5 to 1.5, the content of $[CuL]^+$ cations, $[CuL_2]$ neutral complexes and $[H_2L]^+$ cations practically disappear in the solution. At pH > 1.8 the concentration of H^+ decreases significantly. The concentrations of Cu^{2+} and $[CuL]^+$ cations attain values ≈0.001 and ≈0.003 mol/L, respectively. In the pH range from 1.8 to 2.5

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[2] HySS 2009. Hyperquad Simulation and Speciation, Protonic Software, Leeds (UK), Universita di Firenze, Firenze (Italy), 2009.

[3] Software for the Bruker EMX micro 6/1 spectrometer (*Bruker Corporation*, USA).

[4] IUPAC Stability Constants Database. http://www.acadsoft.co.uk/scdbase/scdbase.htm. Accessed December 03, 2019.

the calculated ratio $C_{[\mathrm{CuL}]^+} / C_{\mathrm{Cu}^{2+}}$ remains constant and equal to 3.5. It is clearly in this range of solution pH, that it is reasonable to consider the equilibrium ionic composition of the cationite.

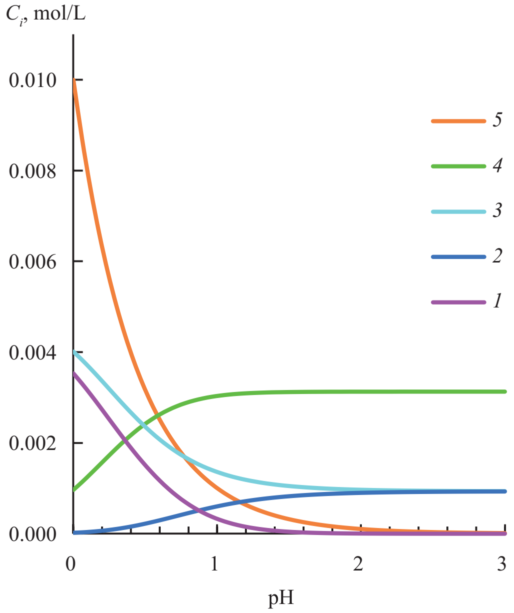

Fig. 2. Dependencies of the concentration of individual components (C_i) on pH of aqueous solutions containing 0.005 mol/L $Cu(NO_3)_2$ and 0.005 mol/L picolinic acid:
(*1*) $C_{[\mathrm{H_2L}]^+}$;
(*2*) $C_{[\mathrm{CuL_2}]}$;
(*3*) $C_{\mathrm{Cu}^{2+}}$;
(*4*) $C_{[\mathrm{CuL}]^+}$;
(*5*) $C_{\mathrm{H}^+} \cdot 10^{-2}$

Fourier transform infrared (FTIR) spectroscopy and ESR spectroscopy were performed, in order to determine the ionic forms of the components contained in the polymer. A clear signal of Cu^{2+} ions is observed in the ESR spectrum of the sample containing copper and picolinic acid. The free radical concentration is $1.65 \cdot 10^{17}$ spin/g, the g-factor is 2.1811 and the line width is 17.5 mTL.

Table 3 shows the wave numbers and the attribution of absorption bands in the FTIR spectra of picolinic acid. It also shows salt $(C_6H_6NO_2)_2SO_4$ containing $[H_2L]^+$ cations, as well as KU-2-8 sulfocationite in Cu^{2+}-form and sulfocationite in mixed Cu^{2+}, $[CuL]^+$-form (brought into equilibrium with a solution containing Cu^{2+} and picolinic acid at pH 2.20, Table 1). A band at 1574 cm^{-1} appears in the spectrum of KU-2-8 sulfocationite in the mixed Cu^{2+}, $[CuL]^+$-form. This corresponds to vibrations of the C=C bond of the pyridine ring [14, 15] according to theoretical calculations [15] by the B3PW91/6-311++G** method. The band at 1377 cm^{-1} corresponds to deformation vibrations of the CH bond [14] and the band at 1297 cm^{-1} to symmetric stretching vibrations of CO [14].

The intense bands at 1724, 1741 cm^{-1} corresponding to the stretching vibrations of the C=O bond in COOH [16, 17], observed in the spectra of picolinic acid and its salt $(C_6H_6NO_2)_2SO_4$, are absent in the spectrum of its complex with Ni(II) and sulfocationite KU-2-8 containing Cu^{2+} and complex $[CuL]^+$.

Thus, analysis of ESR and FTIR spectra confirms that the counterionic composition of KU-2-8 sulfocationite, brought into equilibrium with the solution containing Cu^{2+} and picolinic acid, is represented by Cu^{2+} and $[CuL]^+$ cations. The Cu^{2+} cation in the polymer phase of KU-2-8 sulfocationite, as in aqueous solution [18], interacts with the nitrogen atom of picolinic acid to form $[CuL]^+$ cations.

In the heterogeneous system containing KU-2-8 sulfocationite, aqueous solution of picolinic acid, copper nitrate, and protons, ion exchange reactions take place:

$$2\overline{\mathrm{H}^+} + \mathrm{Cu}^{2+} = \overline{\mathrm{Cu}^{2+}} + 2\mathrm{H}^+, \qquad (5)$$

$$\overline{\mathrm{H}^+} + [\mathrm{H_2L}]^+ = \overline{[\mathrm{H_2L}]^+} + \mathrm{H}^+, \qquad (6)$$

$$\overline{\mathrm{H}^+} + [\mathrm{CuL}]^+ = \overline{[\mathrm{CuL}]^+} + \mathrm{H}^+. \qquad (7)$$

The line above the cations shows that they are part of the polymer phase.

Let us consider the possibility of calculating the composition of the ion exchanger phase. Based on the content of components in the solution, their sorption capacity, and the above-mentioned reactions, we can assume that four competing cations participate in ion exchange on the sulphocationite: Cu^{2+}, $[H_2L]^+$, H^+, $[CuL]^+$. In order to calculate the equilibrium composition of the sulphocationite phase, we used the following system of equations (8):

$$\begin{cases} \dfrac{\overline{C}_{\mathrm{Cu}^{2+}}}{\left(\overline{C}_{\mathrm{H}^+}\right)^2} = k_{\mathrm{Cu/H}} \cdot \dfrac{C_{\mathrm{Cu}^{2+}}}{\left(C_{\mathrm{H}^+}\right)^2} \\ \dfrac{\overline{C}_{[\mathrm{H_2L}]^+}}{\overline{C}_{\mathrm{H}^+}} = k_{\mathrm{H_2L/H}} \cdot \dfrac{C_{[\mathrm{H_2L}]^+}}{C_{\mathrm{H}^+}} \\ \dfrac{\overline{C}_{[\mathrm{CuL}]^+}}{\overline{C}_{\mathrm{H}^+}} = k_{\mathrm{CuL/H}} \cdot \dfrac{C_{[\mathrm{CuL}]^+}}{C_{\mathrm{H}^+}} \\ 2\overline{C}_{\mathrm{Cu}^{2+}} + \overline{C}_{[\mathrm{H_2L}]^+} + \overline{C}_{[\mathrm{CuL}]^+} + \overline{C}_{\mathrm{H}^+} = E, \end{cases} \qquad (8)$$

where $k_{\mathrm{Cu/H}}$, $k_{\mathrm{H_2L/H}}$, $k_{\mathrm{CuL/H}}$ are equilibrium constants (selectivity coefficients of binary ion exchanges) of processes (5), (6), and (7) on KU-2-8 sulfocationite according to [19, 20]. The dimension of component concentration and capacity (E) in the system of equations (8) is mol/L.

Table 3. Wavenumbers of absorption bands in FTIR spectra of picolinic acid, its sulfate $(H_2L)_2SO_4$, complex with Ni(II), and KU-2-8 sulfocationite containing Cu^{2+} and complex $[CuL]^+$, cm^{-1}

Picolinic acid			KU-2-8 in counterionic form		Assignments
HL	$(H_2L)_2SO_4$	$[Ni(II)L_2{\cdot}2H_2O]$ [14]	Cu^{2+}	Cu^{2+}, $[CuL]^+$	
1724s	1741s	–	–	–	Stretching vibrations of the C=O bond in COOH [16, 17]
–	–	1568 FTIR 1575.36 Calculation 1573.44 Calculation	–	1574w	Vibrations of the C=C bond of the pyridine ring [14, 15]
–	–	1374 FTIR 1409 Calculation	–	1377w	Deformation in plane of CH [14]
–	–	1299 FTIR 1291 Calculation	–	1297m	Symmetric CO stretching vibrations [14]
–	–	no data	499s	501s, 490s Doublet	Deformation vibrations of C–H and CCC bonds [15]

Note: s is a strong band, w is a weak band, m is a medium intensity band.

By resolving this system of equations, the calculated dependences of the concentration of cations Cu^{2+}, $[H_2L]^+$, H^+, $[CuL]^+$ in the polymer on the pH of the equilibrium solution containing picolinic acid were obtained at a constant value of $k_{H_2L/H}$, equal to 3.2 (Fig. 3).

Figure 3 shows that as the pH of the solution increases from 1.8 to 2.5, the concentration of Cu^{2+} cations in the polymer slightly increases from 0.87 to 0.93 mol/L. The concentration of $[CuL]^+$ cations remains constant at 0.1 mol/L. The concentration of H^+ decreases from 0.15 to 0.03 mol/L, while the concentration of $[H_2L]^+$ cations is almost zero in the above pH range. The ratio $C_{[CuL]^+} / C_{Cu^{2+}}$ in the polymer, equal to 0.11, remains unchanged. The ratio $C_{[CuL]^+} / C_{Cu^{2+}}$ in the polymer cannot be increased either by increasing the concentration of picolinic acid in solution because of the low solubility of its complexes, or by decreasing the concentration of copper nitrate in solution. The latter will lead to a decrease in the total concentration of Cu^{2+} and $[CuL]^+$ cations in the polymer due to an increase in the concentration of H^+. This is because the concentration of $[H_2L]^+$ cations is practically equal to zero, and the total capacity of the cationite is a constant value. This explains the choice of the concentration of picolinic acid and copper nitrate in solution (0.005 mol/L) in the experiment.

Experimental data on the concentrations of all cations in the cationite within the measurement errors fall within the intervals of calculated compositions (Fig. 3).

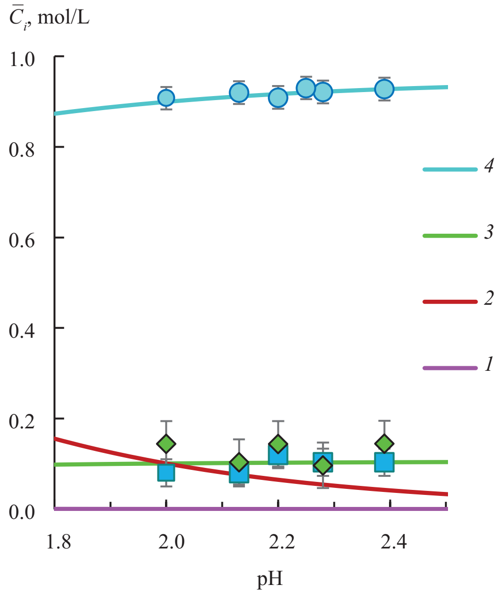

Fig. 3. Dependencies of cations concentration in the polymer on pH of the equilibrium solution: (*1*) $\overline{C}_{[H_2L]^+}$; (*2*) $\overline{C}_{H^+}$; (*3*) $\overline{C}_{[CuL]^+}$; (*4*) $\overline{C}_{Cu^{2+}}$. The lines are the calculations according to the system of equations (8), while the markers are the experiment. The concentrations of Cu^{2+} and $[CuL]^+$ cations in the polymer (blue circle and green rhombus) were obtained from data on the material balance of sorption processes. The concentration of $[CuL]^+$ cations in the polymer (blue square) was obtained from experimental data on the change of the concentration of Cu(II) in the polymer, taking into account the material balance according to the reaction $\overline{Cu^{2+}} + 2[CuL]^+ = 2\overline{[CuL]^+} + Cu^{2+}$

CONCLUSIONS

Thus, equilibrium reactions (1)–(7) do occur in multicomponent heterophase systems consisting of KU-2-8 sulfocationite and aqueous solutions of picolinic acid and copper nitrate. Consequently, it is possible to precalculate the equilibrium ionic compositions of the solution and KU-2-8 sulfocationite by the selectivity coefficients of binary ionic exchanges and the constants of formation of $[H_2L]^+$, $[CuL]^+$ complexes. It is probable that KU-2-8 sulphocationite can be considered as a container for the preparation of drugs based on picolinic acid and Cu^{2+} cations.

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Authors' contributions

H.N. Altshuler – development of the concept and management of scientific work, writing the text of the article.

V.N. Nekrasov – performing an experiment to determine the composition of phases, writing the text of the article.

S.Yu. Lyrshchikov – IR-Fourier spectroscopic study of the polymer phase.

O.H. Altshuler – calculation of equilibrium compositions of the sulfocationite and aqueous solutions, writing the text of the article.

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