ISSN 1070-3632, Russian Journal of General Chemistry, 2014, Vol. 84, No. 13, pp. 2516–2520. © Pleiades Publishing, Ltd., 2014.
Original Russian Text © M.A. Sinyakova, E.A. Semenova, O.A. Gamuletskaya, 2013, published in Ekologicheskaya Khimiya, 2013, Vol. 22, No. 4, pp. 234–238.

Ion Exchange of Copper(II), Lanthanum(III), Thallium(I), and Mercury(II) on the "Polysurmin" Substance

M. A. Sinyakova, E. A. Semenova, and O. A. Gamuletskaya

St. Petersburg State University, Universitetskii pr. 26, St. Petersburg, 198504 Russia
e-mail: kafischem@yandex.ru

Received September 23, 2013

Abstract—Interaction of copper, lanthanum, thallium and mercury salts solutions with an inorganic ion exchanger "polysurmin" was investigated. It was shown that the ion exchanger adsorbs the ions of these metals and exhibits specific selectivity for Hg^{2+} ions demonstrating abnormally high capacity.

Keywords: metal ions, ion exchange, inorganic ion exchangers

DOI: 10.1134/S1070363214130040

INTRODUCTION

Heavy metals are of significant danger for living organisms including people. The category of heavy metals includes more than 40 chemical elements with atomic mass more than 50 Da. So the term is not absolutely corrected but firmly approved in ecological literature [1]; together with term heavy metals, term toxic metals is possible [1, 2]. According to the resolution of the economic committee of United Nations the group of the most danger heavy metals includes mercury, led, cadmium, manganese, nickel, cobalt, vanadium, copper, iron, and zinc. Several of the mentioned metals are vital, for example copper ions play important role in blood formation process, stimulate activity of some ferments, etc. [3]. In the same time copper salts poisoning can cause specific fever accompanied by shivering, body temperature increase, indigestion, change in the blood content. Mercury(II) salts have also strong toxic effect on living organisms: they are able to react with sulfhydryl (or tiol, –SH) groups of proteins including enzymes responded for the proper functioning of the central nervous system. As a result the mercury poisoning causes disorder in hands and legs working, convulsions, giddiness, alteration of periods of nervous excitation and apathy. Many accidents of mass poisoning with mercury salts are known; quite often they lead to lethal end [4]. Thallium(I) salts are also strong poisons [3].

Effective removal of the heavy metal ions from various media is possible with the help of ion-exchange resins of different types. Thus, mercury(II) ions are efficiently adsorbed by the organic ion-exchange resin with sulfhydryl function groups [4], thallium(I) ions can be adsorbed by ferrocyanides including Ferrocin substance [5]. Therefore investigation of adsorption of heavy metal ions on different ion-exchange resins and selection of the most suitable for the ions removal from materials is an important practical task.

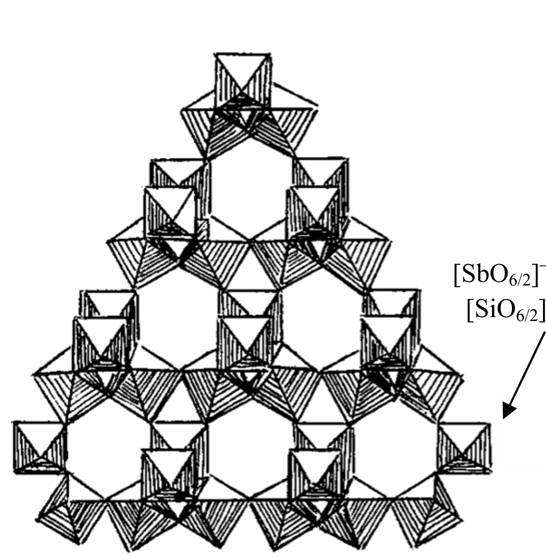

Fig. 1. "Polysurmin" structure.

Adsorption of metal ions from their salts solution

Ion	C^{start}, meq/cm^3	C*, meq/cm^3	G, meq/g	K_{dist}, cm^3/g
Cu^{2+}	0.0250	0.0180	0.70	38.9
	0.0500	0.0385	1.15	29.9
	0.1000	0.0830	1.70	20.5
	0.2000	0.1800	2.00	11.1
La^{3+}	0.0250	0.0135	1.15	85.2
	0.0500	0.0375	1.25	33.3
	0.1000	0.0780	2.20	28.2
	0.2000	0.1755	2.45	14.0
Tl^{+}	0.0198	0.0043	1.55	340.5
	0.0395	0.0230	1.65	71.7
	0.079	0.0539	2.51	46.5
Hg^{2+}	0.0222	0.0000	2.22	–
	0.0478	0.0009	4.69	5211.1
	0.0649	0.0030	6.19	2063.4
	0.0865	0.0178	6.87	386.0
	0.1297	0.0563	7.34	130.4

The object of the study is substance “Polysurmin” that is inorganic ion-exchange resin constituted of mixed antimony and silicon oxyhydrates in a ratio of ~2 : 1. The ion exchange resin may be considered as crystalline antimonic acid in which a part of antimony atoms are isomorphically substituted with silicon atoms. The frame of the substance is constructed from octahedrons $[SbO_{6/2}]^{–}$ and $[SiO_{6/2}]^{2–}$; such form of designation demonstrates that in each cell (in a center) one atom of antimony or silicon is bound with six oxygen atoms and one oxygen atom located in the octahedron corner is bound with two atoms of antimony or silicon. Coordination number 6 is not very typical for silicon but silicon can easily form such cells. Due to large charge of the cell obtained by isomorphic substitution of antimony with silicon, charge of the substance frame on the whole increases together with selectivity of adsorption of multiple-charge ions compared to “pure” antimonic acid (without silicon) [5, 6]. Negative charge of the frame is compensated by the counterions charge.

“Polysurmin” (white powder) is a drug officially recognized by medicine [7]. It is conventionally applied for removal of radioactive ions including Sr^{90} and Ba^{140}.

EXPERIMENTAL

The goal of the work was investigation of the ion-exchange adsorption of copper(II), lanthanum(III), thallium(I) and mercury(II) ions on “Polysurmin.”

The experiments were performed under static conditions. Samples of the ion-exchange resin each of 0.5 g were contacted with aqueous solutions of the investigated metal salts; volume of the solution was in all cases 50 mL, concentration of the salts was varied. Not less than two independent experiments were conducted. Interaction of the ion-exchange resin sample and a solution was proceeded for a period of time necessary for equilibrium establishment (not less than 2 days). After that the ion-exchange resin was separated from the solution, equilibrium concentration of the metal ions in the solution and the solution pH were determined, the ion-exchange resin sample was dried and weighted.

Concentration of Cu^{2+} and La^{3+} ions was determined by trilonometric titration in the presence of

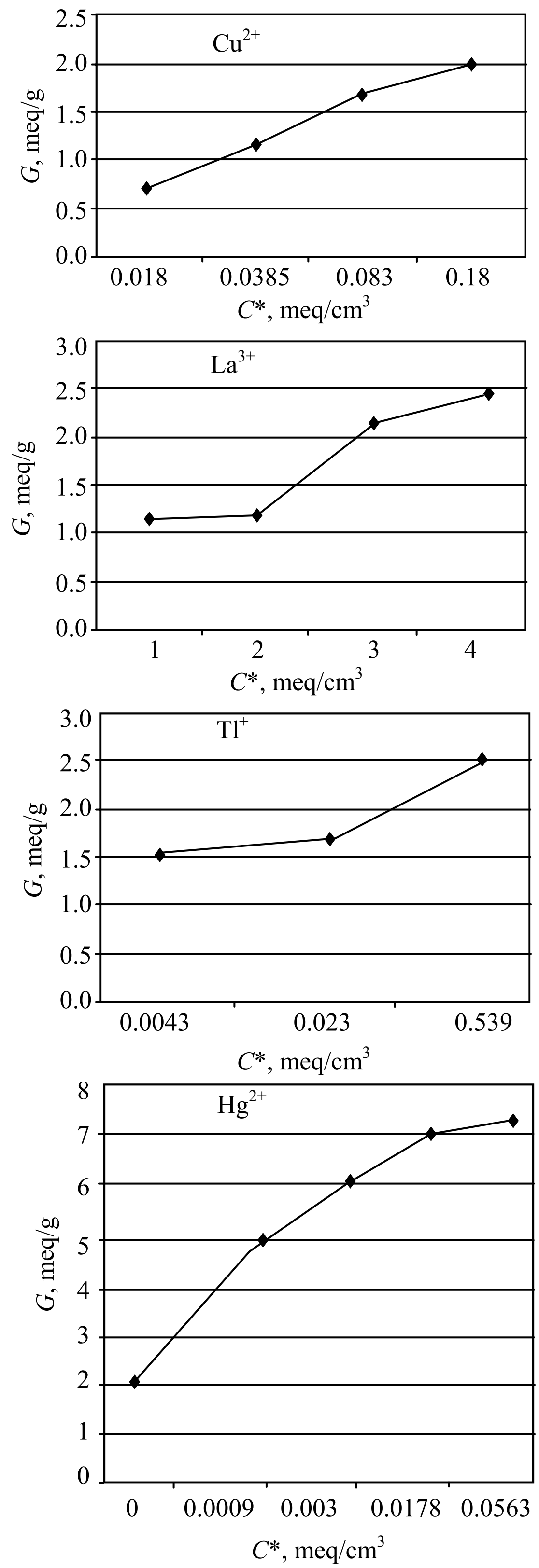

Fig. 2. Dependence of exchange capacity on equilibrium concentration.

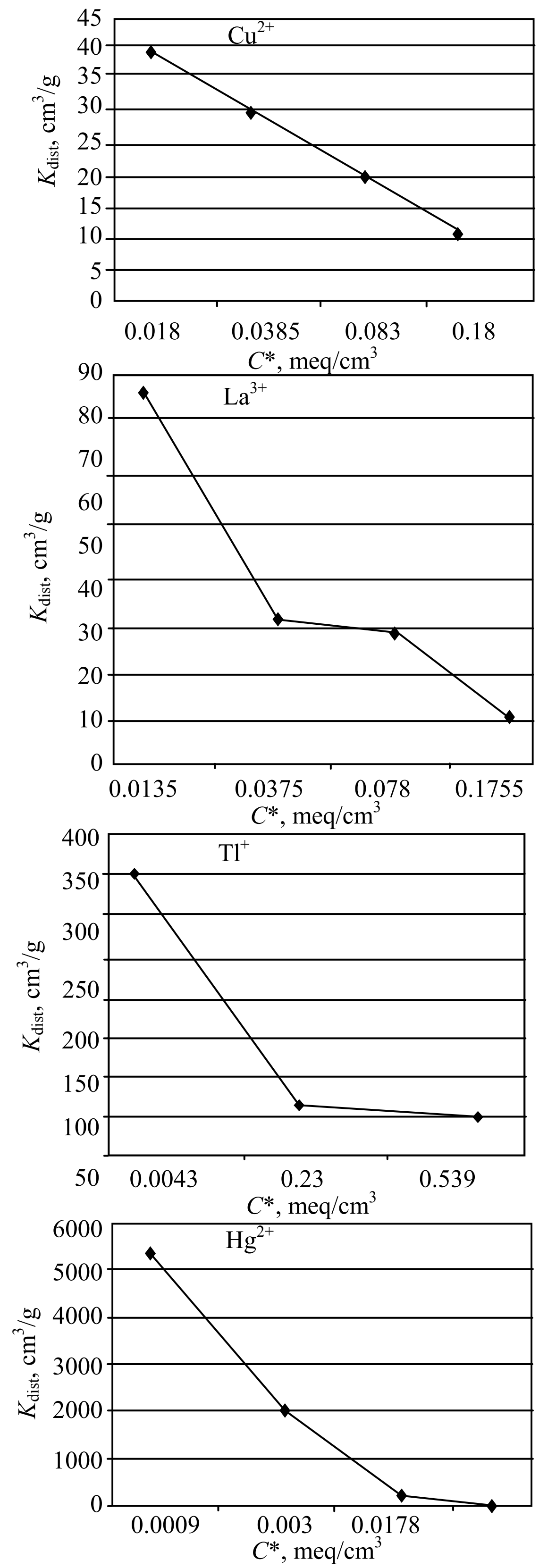

Fig. 3. Dependence of coefficient of distribution on equilibrium concentration.

indicators murexide and xylenol orange respectively. Ions of thallium(I) Tl^+ were precipitated in a form of slightly soluble thallium iodide followed by measuring of iodide excess value. Ions of mercury(II) Hg^{2+} were determined by titration with ammonium rhodanide solution in the presence of ferric ammonium alum as an indicator.

Exchange capacity G, meq/g, was calculated by the equation:

$$G = (C^{\text{start}} - C^*)V/g,$$

where C^{start} and C^* are starting and equilibrium concentrations of Me^{n+} in solution, meq/cm^3; V is a solution volume, cm^3; g is a sample mass, g.

Coefficient of distribution K_{dist} was also calculated by the following equation:

$$K_{\text{dist}} = G/C^*.$$

Coefficient of distribution allows to evaluate the efficiency of ion extraction. The pH control allowed estimation of the metal ion state in a solution; mass change of the resin samples might qualitatively confirm or disprove proceeding of the ion-exchange reaction:

$$n\text{RH} + \text{Me}^{n+} = \text{R}_n\text{Me} + n\text{H}^+,$$

where R is ion-exchange resin.

The rentgenophase investigation of the ion-exchange resin samples was performed on diffractometer Rigaku "MiniFlex-II." The results of the investigations are presented on Figs. 2 and 3.

The observed in the equilibrium solutions pH values correspond to strong acidic medium and indicate existence of the cationic forms of the investigated metals. The samples mass after contact with the solutions increased proportional to amount of the adsorbed metal ions Me^{n+}.

The obtained results are not completely in accordance with the existed conception about "Polysurmin" selectivity [1, 2]. It was expected that lanthanum(III) ions adsorbs better than ions of copper(II) and mercury(II), and the highest selectivity was expected for thallium(I) ions. However the experimentally obtained values of exchange capacity and coefficient of distribution allow disposing the ions in a row:

$$Cu^{2+} < La^{3+} < Tl^+ < Hg^{2+}.$$

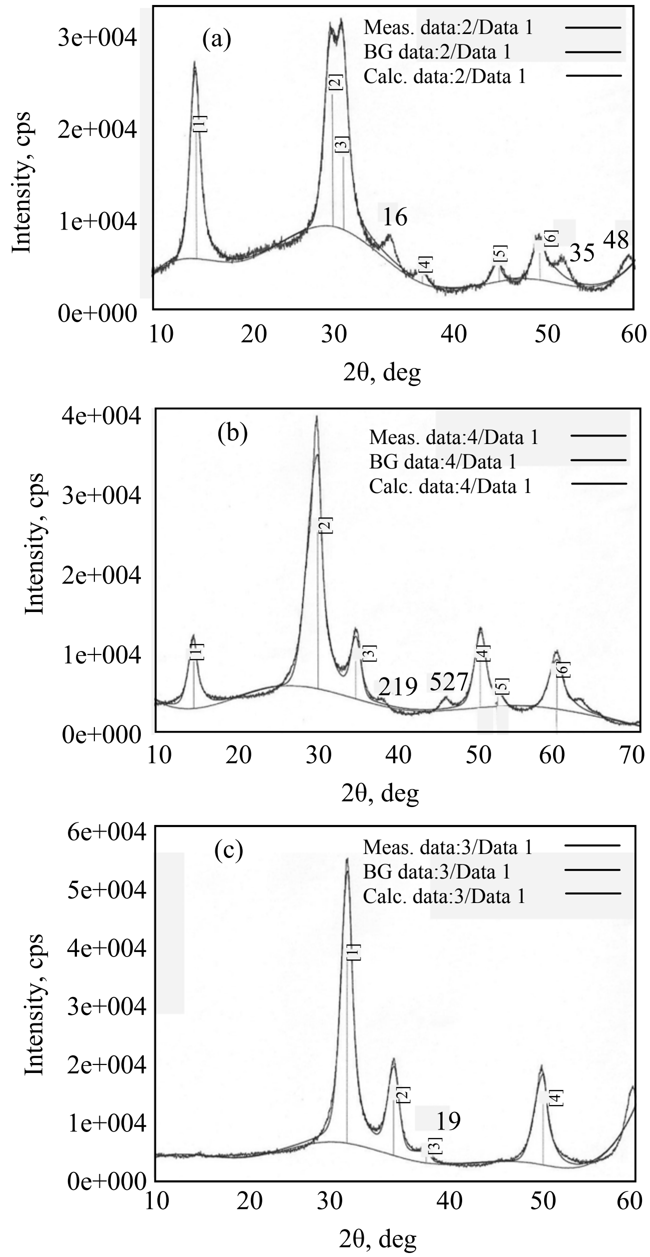

Fig. 4. Diffractograms of the ion-exchange resin samples: (a) at start; (b) with maximal content of Hg^{2+}; and (c) with minimal content of Hg^{2+}.

Mercury undoubtedly takes a special place among the other ions: abnormally high values of exchange capacity are observed at its sorption. It was proposed that a new mercury-containing phase is formed in ion-exchange resin during adsorption process. But the results of rentgenophase investigation did not confirm the supposal. The effects observed on diffractograms can be explained by replacement of H^+ ions with ions

Hg^{2+}; there are no arguments for the presence of new compounds (Fig. 4).

The obtained results proved that “Polysurmin” can be used not only for custom goals (removal of Ba^{2+} and Sr^{2+} ions) but for isolation of thallium and mercury ions.

CONCLUSIONS

(1) For the case of exchange of H^+ ions with the metal ions on “Polysurmin” ion-exchange resin in H-form, a line of sorption selectivity was obtained: $Cu^{2+} < La^{3+} < Tl^+ < Hg^{2+}$.

(2) It was showed that “Polysurmin” ion-exchange resin was exclusively effective for sorption of Hg^{2+} ions revealing high exchange capacity.

ACKNOWLEDGMENTS

This review was performed under financial support by the grant of St. Petersburg State University (12.0.16.2010).

REFERENCES

1. Sadovnikova, L.K., Orlov, D.S., and Losanovskaya, I.N., *Ecologiya i okhrana okruzhayushchei sredy pri khimicheskom zagryaznenii* (Ecology and Environmental Protection at Chemical Contamination), Moscow: Vysshaya Shkola, 2006.
2. Sinyakova, M.A., *Cand. Sci. (Chem.) Dissertation,* St. Petersburg, 1999.
3. *Vrednye veshchestva v promyshlennosti* (Harmful Substances in Industry), Lazarev, V.N., Ed., Moscow: Khimiya, 1965, vol. 2.
4. Leikin, Yu.A.*, Osnovy ekologicheskogo normirovaniya* (Basics of Ecological Standardization), Moscow: D.I. Mendeleev RKhTU, 2009.
5. *Ionity v khimicheskoi tekhnologii* (Ion-Exchange Resins in Chemical Technology), Nikol’skii, B.P. and Romankov, P.G., Eds., Leningrad, 1982.
6. Belinskaya, F.A., *Obshchie zakonomernosti obmena ionov na neorganicheskikh ionoobmennykh materialakh* (General Principles of Ions Exchange on Inorganic Ion-Exchange Materials), Leningrad: Leningrad. Gos. Univ., 1984.
7. *Temporary Compendial Paper on “Polysurmin,”* no. 42-574-76 dated by June 25, 1976.