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LETTERS TO THE EDITOR

Liquid Extraction of Metal Ions with Phosphonate Derivatives of Amino Acids

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Study of liquid and membrane extraction [1] is important in view of development of processes of recovery, concentration, and separation of rare and trace elements. We have earlier demonstrated a rapid interphase and transmembrane transport of certain metal ions aided by neutral aminophosphine oxide carriers [2]. Furthermore, we have shown the application of lipophilic phosphorylated derivatives of natural amino acids as membrane extracting agents [3].

In this work we studied properties of *N*-bis(2-ethylhexyloxy)phosphorylmethyl derivatives of sarcosine (**I**) and β-alanine (**II**) as new agents for liquid extraction of Cu(II), Fe(III), Ni(II), and Co(II) ions from nitric acid aqueous solutions. Degree of extraction of the metal ions with compound **I** as a function of pH is tabulated below.

The obtained results show the increasing degree of the metal ions extraction with increasing pH of the aqueous phase, the extracting efficiency decreasing in the Cu(II) > Fe(III) > Ni(II) ≈ Co(II) series. The observed trend was typical of metal ions extraction via the cation-exchange mechanism. Noteworthily, copper could be extracted even from the strongly acidic media.

The lower efficiency of iron ions extraction in comparison with that of copper ions looked unusual. Indeed, most phosphorylated agents have exhibited better extraction of Fe(III) ions; for instance, tributyl phosphate extracts Fe(III) but not Cu(II) [4]. The observed feature was due likely to the contribution of the amino acid fragment to the complex formation: copper(II) is known to form strong complexes with amino acids [5].

Leaching solutions containing sulfuric acid are important objects of copper hydrometallurgy. We studied the effect of pH of the sulfuric acid-containing aqueous phase pH on degree of extraction of the ions with 0.05 mol/L solution of the extracting agents in chloroform. The results demonstrated that copper(II) ions could be extracted with similar efficiency from both sulfuric and nitric acid media: in both cases pH of semiquantitative extraction was close to 0.5.

pH	0.39	0.55	0.90	1.00	1.80	2.90	3.20
Fe (III)	2.99	31.73	37.90	54.70	99.22	99.53	99.07
Cu (II)	54.01	95.65	98.64	99.38	99.70	99.85	99.90
Co (II)	7.07	5.18	7.20	5.00	3.80	26.78	39.14
Ni (II)	5.62	4.42	7.50	4.70	3.80	17.90	43.80

The derivative **II** was significantly less efficient in the metals extraction: copper extraction was quantitative only at pH > 5. That could be attributed to lower stability of complexes of α-amino acids as compared to their β-analogs. For example, the stability constant of copper(II) complex with glycine is 15.4, being 12.9 in the case of β-alanine 12.9 [6].

To summarize, the aminophosphoryl derivative of sarcosine, **I**, is a promising extracting agent selective with respect to Cu(II) ions; it can be used to separate Cu(II) ions from Fe(III), Ni(II), and Co(II) via extraction from the strongly acidic medium. Details of the extraction process will be reported separately in the forthcoming paper.

Preparation and characterization of derivatives **I** and **II** [7] and the experimental procedures of the membrane processes study [8] have been described elsewhere.

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REFERENCES

1. Zhongmao, G., *Membrane Sci. Technol*., 2003, vol. 23, p. 214.
2. Cherkasov, R.A., Garifzyanov, A.R., Galeev, R.R., Kurnosova, N.V., Davletshin, R.R., and Zakharov, S.V., *Russ. J. Gen. Chem*., 2011, vol. 81, no. 7, p. 1464. DOI: 10.1134/S1070363211070103.
3. Cherkasov, R.A., Garifzyanov, A.R., Koshkin, S.A., and Davletshina, N.V., *Russ. J. Gen. Chem*., 2012, vol. 82, no. 8, p. 1453. DOI: 10.1134/S10703632120802IX.
4. *Spravochnok khimika* (Chemist's Handbook), Nikol'skii, B.P., Ed., Leningrad: Khimiya, 1967, vol. 4, p. 93.
5. Childs, C.W. and Perrin, D.D., *J. Chem. Soc*., 1969, p. 1039. DOI: 10.1039/j19690001039.
6. Albert, A., *Biochem. J.,* 1950, vol. 47, p. 531.
7. Garifzyanov, A.R., Davletshina, N.V., Koshkin, S.A., Valeeva, M.S., and Cherkasov, R.A., *Russ. J. Gen. Chem*., 2014, vol. 84, no. 8, p. 1051. DOI: 10.1134/S107036214060345.
8. Cherkasov, R.A., Garifzyanov, A.R., Bazanova, O.B., and Leontjeva, S.V., *Russ. J. Gen. Chem*., 2011, vol. 81, no. 10, p. 2080. DOI: 10.1134/S1070363211100070.