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LETTERS TO THE EDITOR

To the 85th Anniversary of birthday of late Yu.G. Gololobov

Synthesis and Membrane-Transport Properties of New Lithium-Selective Extracting Agent, Tris(*O*,*O*-diamylphosphorylmethyl)amine

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Development of new technologies of lithium extraction from relatively poor unconventional sources (mineral and hydrothermal waters) has become important in view of the increasing demand of modern industry for metal lithium and its compounds. Membrane extraction can serve as cost-efficient for retrieval of the target components from such solutions. Since hydrothermal waters are rich in sodium and potassium ions, elaboration of lithium extraction methods should include the development of approaches to separate lithium from these accompanying elements [1, 2].

We have earlier studied the process of selective membrane extraction of lithium ions from the solutions of alkali metals salts using the synergetic mixture of the carriers: *N*,*N*-bis(dihexylphosphorylmethyl)octylamine and didecylthiophosphorus or -dithiophosphorus acid [3].

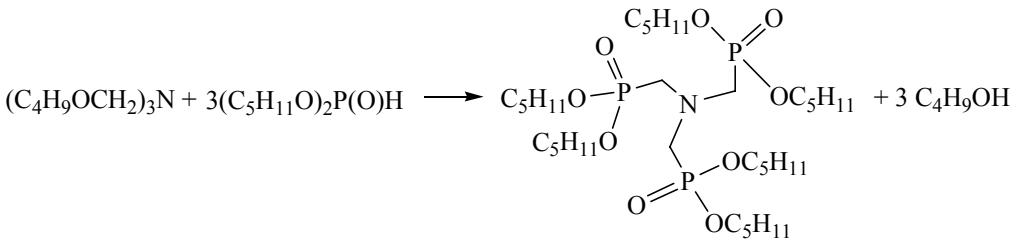
Here we report on investigation of selective membrane extraction of lithium ions from their mixtures with other alkali metal ions (sodium, potassium, rubidium, and cesium) using a synergetic mixture of tris(*O*,*O*-diamyl-phosphorylmethyl)amine and *O*,*O*-bis-(2-ethylhexyl)monothiophosphorus acid (Scheme 1).

It was specially demonstrated that the lithium ion transport was not efficient in the absence of the acid component, the flow being no more than 10^{-4} mol m^{-2} min^{-1}; that evidenced the participation of the acid anion in the formation of the complex of the $[(C_5H_{11}O)_2P(O)CH_2]_3NLi^+ \cdot (2\text{-}C_2H_5C_6H_{12}O)_2PSO^-$ type.

In a typical antiport experiment the carriers solution in kerosene acted as the membrane phase. Concentration of the alkali metals in the feed solution ranged from 0.02 to 0.1 mol/L, and aqueous solution of sulfuric acid (0.2 mol/L) acted as the stripping phase.

It was demonstrated that the optimal ratio of the amine and the acid components in the extracting mixture was 11 : 1, the concentrations in the

Scheme 1.



The transmembrane flow (Π) and the selectivity coefficients (*S*) with respect to the alkali metal ions at their different concentration in the feed solution

c_{M^+}, mol/L[a]	Π × 10^{-3}, mol m^{-2} min^{-1}					*S*			
	Li	Na	K	Rb	Cs	Li/Na	Li/K	Li/Rb	Li/Cs
0.1	4.16	0.78	0.52	0.38	0.52	5.32	7.98	10.79	7.98
0.05	2.76	0.91	0.70	0.57	0.52	3.04	3.91	4.86	5.28
0.02	1.87	0.65	0.46	0.34	0.33	2.89	4.02	4.71	5.69

[a] The metal concentration in the taking solution.

membrane phase being 0.25 and 0.022 mol/L, respectively. The tabulated results confirmed the consistent decrease in the lithium ion flow by 1.5 times when its concentration in the feed phase was reduced from 0.1 to 0.02 mol/L. The flows of other alkali ions were not significantly changed under the same conditions. The variation of the selectivity coefficients at the change in the metal concentrations could point at the formation of several types of complexes involving several molecules of the ligands (carriers) in the mem-brane phase.

The listed data demonstrated that the membrane was not saturated with lithium over the studied concentrations range; furthermore, the selectivity towards lithium membrane transport was somewhat improved with the increasing metal concentration. The latter could be due to the enhanced competition during the metal ions sorption at the feed solution/membrane interphase boundary.

In summary, the synergetic mixture of the trisphosphorylamine and the monothioacid was markedly selective and could be regarded as a promising membrane extracting agent for recovery of lithium from various sources.

Tris(*O*,*O*-diamylphosphorylmethyl)amine was prepared via a method reported elsewhere [4], the reaction of trisbitoxymethylamine with diamyl phosphoric acid. *O*,*O*-Bis-(2-ethylhexyl)monothiophosphorus acid was prepared via a method described in [5]. The transmembrane flows were measured as described in [3].

Tris(*O*,*O*-diamylphosphorylmethyl)amine. A mixture of 77.00 mmol (17.09 g) of diamyl phosphite and 23.00 mmol (6.32 g) of tris(butoxymethyl)amine was heated at 120°C during 3 h, butanol being simultaneously distilled off at 20 mmHg. The reaction course was monitored by ^{31}P NMR spectroscopy. Excess of diamyl phosphite was removed via heating in a vacuum to a constant mass. Yield 15.90 g (96%), colorless viscous oil, n_D^{20} 1.4522. IR spectrum, ν, cm^{-1}: 1000 s (POC), 1150 s (P=O). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 0.90 t (18H, C<u>H</u>$_3$CH$_2$, $^3J_{HH}$ 6.5 Hz), 1.28–1.41 m [24 H, (C<u>H</u>$_2$)$_2$], 1.60–1.67 m (12H, C<u>H</u>$_2$), 3.31 d (6H, PC<u>H</u>$_2$N, $^2J_{PH}$ 10.9 Hz), 4.02–4.09 m (6H, CH$_2$C<u>H</u>$_2$O). ^{13}C–{H} NMR spectrum ($CDCl_3$), δ_C, ppm: 13.78 (<u>C</u>H$_3$CH$_2$), 22.12 (CH$_3$<u>C</u>H$_2$), 27.55 (CH$_3$CH$_2$<u>C</u>H$_2$), 30.14 (<u>C</u>H$_2$CH$_2$O), 62.1 d (P<u>C</u>H$_2$N, $^1J_{CP}$ 156.7 Hz), 65.94 (CH$_2$<u>C</u>H$_2$O). ^{31}P NMR spectrum: δ_P 23.60 ppm. Mass spectrum (ESI-HRMS): *m*/*z* 720.4495 $[M + Na]^+$ (calculated: 720.4493).

^{1}H, ^{31}P, and ^{13}C–{^{1}H} NMR spectra were recorded using a Bruker AVANCE III spectrometer at 400, 162, and 100 MHz, respectively. Mass spectrum was measured using an AB Sciex TripleTOF 5600 high-resolution spectrometer equipped with a DuoSpray ionization source in the positive ionization mode (5500 V, air as the spray gas). IR spectra of thin films were registered using a Perkin Elmer Spectrum Two spectrometer.

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REFERENCES

1. Goyette, M.L. Longin, T.L., Noble, R.D., and Koval, C.A., *J. Membr. Sci*., 2003, vol. 212, no. 1, p. 225.
2. Ma, P. and Chen, X., *Sep. Sci. Technol*., 2000, vol. 35, no. 15, p. 2513.
3. Garifzyanov, A.R., Davletshina, N.V., Garipova, A.R., and Cherkasov, R.A., *Russ. J. Gen. Chem*., 2014, vol. 84, no. 2, p. 285. DOI: 10.1134/S1070363214020224.
4. Prishchenko, A.A., Livantsov, M.V., Lorents, K.L., Papsuev, M.Yu., Grigoriev, E.V., and Luzikov, Yu.N., *Russ. J. Gen. Chem*., 1994, vol. 64, no. 8, p. 1171. DOI: 1181/35400005171989.0150.
5. Kormachev, V.V. and Fedoseeva, M.S., *Preparativnaya khimiya fosfora* (Preparative Chemistry of Phosphorus), Mosocw: Perm, Ural. Otd. Ross. Akad. Nauk, 1992, p. 457.