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Sinergetic Membrane Extraction of Lithium Ions with New Organophosphorus Carriers

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Abstract—We have studied membrane transport properties towards alkali metal ions of sinergetic mixtures of organophosphorus carries, *N,N*-bis(dihexylphosphorylmethyl)octylamine and didecylthiophosphorus or didecyldithiophosphorus acids. The influence of main parameters of extraction (pH of the feed phase as well as concentration and ratio of the carriers in the membrane) on the membrane transport rate and selectivity with respect to lithium has been analyzed. Conditions of efficient and selective (to separate K^+ and Na^+) membrane extraction of Li^+ have been established. Advantages of the studied systems in comparison with some previously known ones are demonstrated.

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Due to depletion of natural metals sources development of methods of metals extraction, concentration, and separation is definitely a topical issue. Recently lithium extraction has become especially important. Its extraction from the main natural source, salty lakes brine, is complicated due to significant amounts of the accompanying elements, sodium and potassium. The emerging requirement in developing environmentally safe methods of used lithium batteries utilization makes the above-stated engineering problems still more important.

Modern methods of processing natural lithium sources and its extraction from the exhaust materials are largely based on membrane technologies, including lithium transport through impregnated liquid membranes [1–3]. The following phosphorus acid derivatives have shown fairly efficient properties of transmembrane carriers of lithium ions: 2-ethylhexylphosphonic acid and its esters [4], lipophilic alkyl esters of phosphonic acid [5], tributylphosphate and trioctylphosphine oxide [6], mono- and dithiophosphates Cyanex [7]. Highly efficient lithium extractants include the so called sinergetic carriers: mixtures of organic compounds of different nature, including organophosphorus ones [8–10]. Due to sinergetic effect exhibited by such multicomponent mixtures, they are widely applied in development of efficient technologies of rare and scattered elements extraction [8–10]. Sinergetic carriers are also applicable to extraction of Li^+ and its separation from other alkali metals [3–7]. Despite definite progress in the field, development of new efficient and selective liquid extractants and membrane carriers has remained a topical issue so far [11, 12].

We have recently investigated applicability of various aminomethylphosphine oxides in membrane extraction of ions of rare and scattered elements [13–15]. In particular, we have demonstrated high efficiency and selectivity of membrane transport of scandium and lanthanides ions with *N,N*-bis(dihexylphosphorylmethyl)octylamine **I**, these ions transport being much faster than that of other groups **II** and **III** metal ions. Furthermore, we have shown that proper phosphorylamine **I** is not efficient in membrane extraction of alkali ions: they are practically not extracted from the the feed phase. In this work we studied efficiency of mixed extracting agents including the amine **I** in membrane extraction of Li^+, Na^+, and K^+ under conditions of active membrane transport via the antiport method. In this case the metal ions transports occurred due to excess of hydrogen ions in the receiving phase.

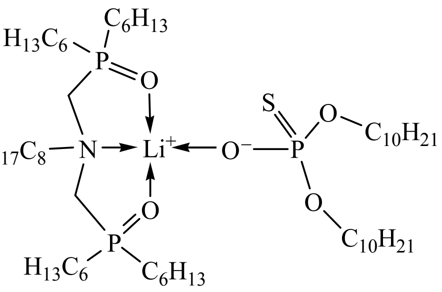
As was shown in [7], salts of higher dialkylthiophosphorus acids could efficiently extract heavy metal ions. An important advantage of those agents was that their salts with alkali metals were infinitely soluble in nonpolar organic solvents, in particular, in petroleum ether and kerosene.

Preliminary test runs revealed that alkali ions transport through membranes impregnated with 0.2 mol/L solution of didecylthiophosphorus acid **II** in 5,8,11-trioxy-*n*-heptadecane was inefficient, probably due to low stability of the complexes formed in such extraction system. On the contrary, the low extracting ability of amine **I** towards alkali ions was likely due to the formation of extremely stable complexes [13]. In view of the above-mentioned, we studied the extraction properties of **I** + **II** mixture.

In the typical experiment the feed phase was a mixture of aqueous solutions of lithium, sodium, and potassium hydrophosphates (0.1 mol/L), and the receiving phase contained 0.005 mol/L of sulfuric acid. Kerosene was used as membrane medium, as it was immiscible with water, inert, readily available, and had sufficiently high boiling point; polytetrafluoroethylene film was used as membrane.

In the complexes with metal ions, the phosphorylamine **I** acted as tridentate ligand [13–15], therefore we assumed that in the presence of thiophosphorus acid in the organic medium the mixed chelate complex of lithium with both the organophosphorus ligands could be formed (**A**).

Figure 1 shows the kinetic curves of alkali metals ion transport through membrane phase containing mixture of phosphorylamine **I** and acid **II**. Lithium transport was evidently more efficient as compared with those of sodium and potassium.



A

In order to optimize the membrane phase composition, we measured Li^+ flow at varied total concentration of **I** + **II** mixture and at varied components ratios (Table 1). The best transport properties were found in the cases of mixtures nos. 1 and 2.

The selectivity coefficients (calculated as the ratio of lithium flow to that of sodium or potassium) in the cases of all studied systems were relatively low (2.0 to 9.3). That could possibly result from surfactant properties of acid **II**. Indeed, as the transport occurred due to pH gradient, the membrane components should not be efficient surfactants, otherwise membrane leakage could occur via micellar water transfer.

We attempted to solve the problem by replacing acid **II** by didecyldithiophosphorus acid (**III**). In the acidic group of **III** the polar and easily deprotonated oxygen atom was absent. Nevertheless, the **I** + **III** system could still extract lithium in the form of complex similar to **A**.

Figure 2 contains examples of kinetic curves of alkali metal ions transfer by mixtures of **I** and **III** at

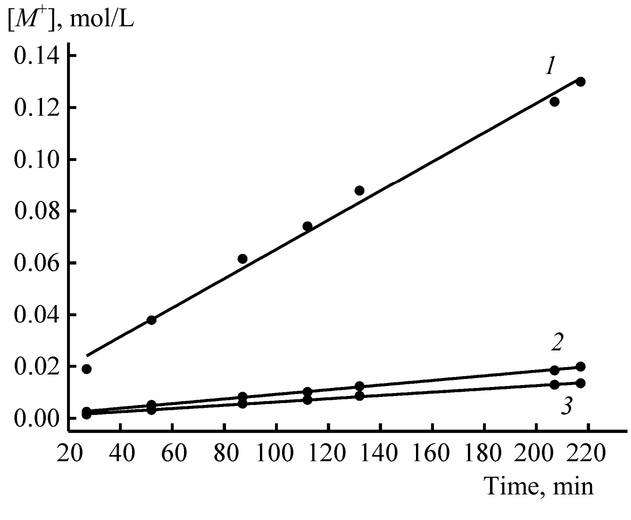


Fig. 1. Kinetics of Li^+ (*1*), Na^+ (*2*), and K^+ (*3*) transport by sinergetic mixture of phosphorylamine I and acid **II** at pH = 7.62, $c_{\mathrm{I}} = 0.25$ mol/L, and $c_{\mathrm{II}} = 0.034$ mol/L.

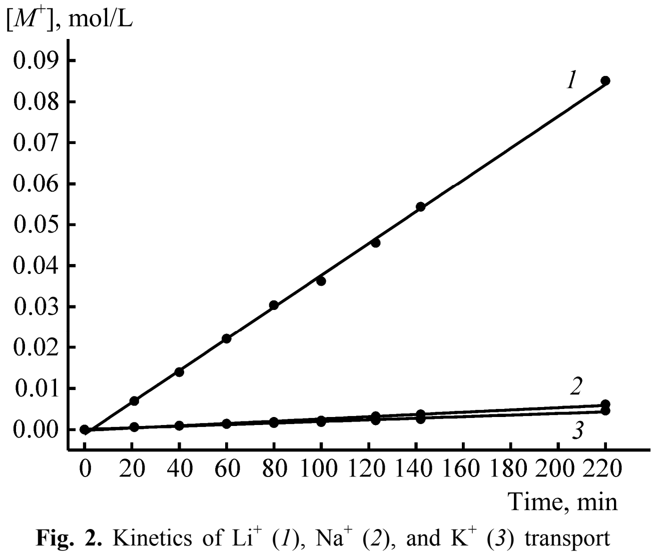


Fig. 2. Kinetics of Li^+ (*1*), Na^+ (*2*), and K^+ (*3*) transport with sinergetic mixture of phosphorylamine **I** and acid **III** at pH = 6.97, $c_{\mathrm{I}} = 0.38$ mol/L, and $c_{\mathrm{III}} = 0.062$ mol/L.

Table 1. Flow F ($n = 3$, $P = 0.95$) and selectivity S of Li^+ transport at varied concentrations of phosphorylamine **I** and acid **II** in the mixture

Run no.	c_{I}, mol/L	c_{II}, mol/L	pH_{rel}	Δc^a	Selectivity coefficient		$F \times 10^3$ mol m^{-2} min^{-1}
					$S_{Li/Na}$	$S_{Li/K}$	
1	0.25	0.034	7.62	5.9	6.6	9.3	6.6 ± 0.5
2	0.25	0.062	7.65	8.0	6.8	9.1	9.1 ± 0.8
3	0.25	0.130	7.51	4.0	4.7	4.9	4.5 ± 0.4
4	0.25	0.250	7.86	5.6	3.7	4.6	6.3 ± 0.5
5	0.13	0.130	7.71	4.0	4.7	4.9	4.6 ± 0.3
6	0.38	0.062	7.61	0.7	2.0	2.8	0.8 ± 0.09

[a] Kinetics of Li^+ concentration change in the feed phase, $\partial c(Li^+)/\partial t \times 10^4$, mol min^{-1} L^{-1}.

Table 2. Flow F ($n = 3$, $P = 0.95$) and selectivity S of Li^+ transport at varied pH of the feed phase: $c_{\mathrm{I}} = 0.38$ mol/L, $c_{\mathrm{III}} = 0.062$ mol/L

Run no.	pH_{rel}	Δc^a	Selectivity coefficient		$F \times 10^3$ mol m^{-2} min^{-1}
			$S_{Li/Na}$	$S_{Li/K}$	
1	4.00	0.74	12	19	0.8 ± 0.08
2	4.99	1.6	15	27	1.8 ± 0.1
3	5.49	2.2	16	24	2.5 ± 0.1
4	5.99	3.2	12	18	3.7 ± 0.2
5	6.50	3.7	13	28	4.2 ± 0.4
6	6.97	3.9	14	20	4.4 ± 0.3
7	7.63	4.6	13	23	5.2 ± 0.5
8	8.30	4.1	13	18	4.7 ± 0.3
9	9.50	1.7	12	20	1.9 ± 0.1

[a] Kinetics of Li^+ concentration change in the feed phase, $\partial c(Li^+)/\partial t \times 10^4$, mol min^{-1} L^{-1}.

pH = 6.97. As seen from the plots, lithium transport was much faster as compared with that of other alkali metals. Hence, the introduction of acid **III** into the membrane phase enhanced the selectivity coefficients towards lithium ions (up to 20–23) at fairly high lithium ions flow, of 4.4–5.2 mmol m^{-2} min^{-1}.

In order to optimize the extraction conditions with respect to selectivity, we measured the transport flows of alkali ions at varied pH of the feed phase at the constant carriers concentration in the membrane (Table 2).

The highest Li^+ flow was observed at pH = 6.5–8.5; under these conditions the highest selectivity towards lithium was achieved. The rate of change of lithium concentration in the feed phase (proportional to the ions flow) revealed the typical domelike shape with maximum at the optimal extraction conditions (Fig. 3).

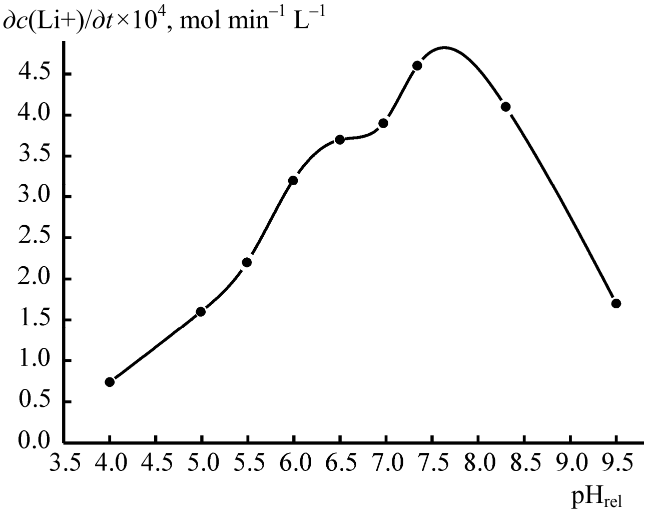


Fig. 3. Kinetics of Li^+ concentration change as a function of the feed phase pH.

The relatively low lithium flow at low pH was likely due to the competing action of protons excess that were extracted along with Li^+. Slowing down of Li^+ in the basic medium could be due to acid **III** leaching from the membrane phase.

The obtained results showed that the liquid membranes based on porous tetrafluoroethylene film impregnated with solution of the **I** + **II** or **I** + **III** mixtures in kerosene were capable of selective transport of lithium in the presence of sodium and potassium ions. The highest lithium ions flow was achieved in the case of membrane containing **I** + **III** mixture at pH of 5–8. Under these conditions the selectivity of lithium extraction with respect to sodium and potassium was of 12–16 and 18–28, respectively.

As far as the acids **II** and **III** are compared, using the **I**+**III** sinergetic mixture we could achieve better selectivity towards lithium, however, its ions flow was several times lower than in the case of **I** + **II** system. Nevertheless, in both cases the studied transmembrane carriers demonstrated efficient extraction of lithium from weakly acidic or neutral solutions via the antiport mechanism. At the same time, the membrane system described in [3] (based on β-diketones and trioctylphosphine) extracted lithium ions exclusively from basic solutions. As typical pH of majority of the underground ore waters and brine water is close to neutral, the membrane systems developed in this work seem more promising for practical applications.

EXPERIMENTAL

N,N-Bis(dihexylphosphorylmethyl)octylamine (**I**) was prepared according to [16], didecylthiophosphorus acid (**II**) and didecyldithiophosphorus acid (**III**) were prepared as described in [17].

The carriers solutions in organic solvents were prepared by weighing. Solutions of inorganic substrates were prepared by dissolution of the weighed amount of nitrate, perchlorate, or hydrophosphate of the studied metal (pure or chemically pure grade) in bidistilled water.

Membrane extraction was studied using the classical vertical cell with moving cylinder. The receiving phase was put into the internal vessel, its bottom being impregnated liquid membrane. Volumes of the feed and the receiving phases were 100 and 25 mL, respectively; initial concentrations of alkali ions were of 0.1 mol/L. Levels of the feed and the receiving phases were the same [18]. Aqueous solution of sulfuric acid (0.05 mol/L, chemical pure grade) was used as the receiving phase. The membranes were prepared by longitudinal stretching of the low-temperature sintered fluoroplast tape. Ions flow was calculated using Visual UMNIK-2002 software [13]. Concentrations of the alkali metals were measured with PFM U4.2 flame photometer.

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