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LETTERS TO THE EDITOR

Membrane Transport of Alkali Metals with Phosphorylmethyl Derivatives of Amino Acids

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Membrane technologies, including transport of alkali metal ions through impregnated liquid membranes [1] are widely utilized nowadays in processing of sources and wastes of alkali metals, above all lithium. We have earlier demonstrated that lipophilic α-aminophosphine oxides are efficient carriers of rare and trace elements through liquid supported membranes; however, alkali metal ions are retained in the feed aqueous phase under conditions of the membrane extraction [2]. Herein we present the data on membrane extraction of alkali metal ions (Li, Na, and K) using the lipophilic bismethylphosphorylated derivatives of glycine (**I**, n = 1) and β-alanine (**II**, n = 2) $[(C_8H_{17})_2P(O)CH_2]_2N(CH_2)_nCOOH$ as transmembrane carriers. The measured transmembrane flows are shown in the table.

According to the obtained data, both amino acid derivatives acted as efficient transmembrane carriers of all alkali metal ions from neutral and weakly alkaline feed phases, in contrast to the earlier studied neutral aminophosphoryl extracting agents. At the same time, no selectivity towards lithium transport (earlier demonstrated when using the synergetic carrier, equimolar mixture of *N*,*N*-bis(dihexylphosphorylmethyl)-octylamine and phosphorus dioctylmonothioacid or dioctyldithioacid [3]) was observed in this work. The carrier **II** was more efficient in the alkaline medium, giving rise to six-fold higher transport flows as compared to the carrier **I** under the same conditions. When pH of the feed phase was decreased, all the transport flows aided by compound **I** incresed almost three times; again, no selectivity towards any of the ions was observed. Noteworthily, the ability of the studied carriers towards membrane extraction of the alkali metal ions from neutral medium is their important advantage over the membrane system based on β-diketones and trioctylphosphine oxide, the latter being capable only of lithium extraction from the alkaline solutions [4]. As pH of underground and sea

Transmembrane flow (P, mol m^{-2} min^{-1}) of Li, Na, and K ions at different pH of the feed phase (c = 0.1 mol/L)

Carrier	pH	Δc[a]			$P \times 10^{-3}$		
		Li	Na	K	Li	Na	K
I	7.47	2.38	2.16	2.19	2.70	2.45	2.49
	9.35	0.90	0.95	0.92	1.02	1.08	1.05
II	7.47	1.44	1.81	2.09	1.63	2.05	2.37
	9.43	6.14	5.80	5.98	6.96	6.57	6.78

[a] Change rate of the metal concentration in the feed phase $dc_{M^+}/d\tau \times 10^4$, mol/min.

waters is generally close to neutral, the membrane transport systems described in this contribution are promising in view of the practical applications.

Membrane transport through the impregnated membranes was carried out in the cell constructed of two beakers. The outer beaker (the constant-temperature Dewar vessel) was filled with the feed phase. The inner Teflon beaker (the impregnated liquid membrane, low-temperature fluoroplastic film saturated with the carrier solution in kerosene, acting as its bottom) was filled with the receiving phase. The ions concentration was monitored by means of conductometry.

***N*-Methylphosphorylated amino acids** *(general procedure).* A mixture of 0.009 mol of the amino acid, 0.0189 mol (0.567 f) of paraformaldehyde, 0.018 mol (4.94 g) of dioctyl phosphinite, 0.0045 mol of the amino acid hydrochloride, and 100 mL of acetonitrile was refluxed during 3 h. The unreacted amino acid was filtered off, and the filtrate was evaporated. The residue contained the target phosphorus-containing amino acids.

***N*,*N*-Bis(dioctylphosphorylmethyl)-β-alanine (I).** Yield 81%, white amorphous substance, mp 98°C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 0.89 t (12H, CH_3, $^3J_{HH}$ 12.0), 1.28–1.88 m [56H, $(CH_2)_7P$], 2.53 t (2H, $C\underline{H}_2COOH$, $^3J_{HH}$ 8.0), 3.03 d (2H, CH_2P, PCH_2N, $^2J_{HP}$ 4.0), 3.15 t (2H, NCH_2, $^3J_{HH}$ 12.0). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm (*J*, Hz): 14.09 (CH_3), 21.59 d ($\underline{C}H_2CH_2CH_2P$, $^2J_{CP}$ 4.0), 22.63 ($CH_3\underline{C}H_2$), 26.87 d (PCH_2, $^1J_{CP}$ 64.0), 29.12 ($CH_3CH_2CH_2\underline{C}H_2$ + $CH_3CH_2CH_2CH_2\underline{C}H_2$), 31.24 d ($\underline{C}H_2CH_2P$, $^2J_{CP}$ 14.0), 31.64 ($\underline{C}H_2COOH$), 31.79 ($CH_3CH_2\underline{C}H_2$), 53.68 d (PCH_2N, $^1J_{CP}$ 72.0), 54.37 (NCH_2), 173.7 (COOH). ^{31}P–{H} NMR spectrum: δ_P 49.80 ppm. Mass spectrum (ESI-HRMS): *m*/*z* 684.5229 $[M + Na]^+$ (calculated: 684.5226). Found, %: C 67.28; H 11.91; O 9.72; N 2.01; P 9.08. $C_{37}H_{77}NO_4P_2$. Calculated, %: C 67.13; H 11.72; O 9.67; N 2.14; P 9.36.

***N*,*N*-Bis(dioctylphosphorylmethyl)glycine (II).** Yield 84%, colorless viscous oil. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 0.89 t (12H, CH_3, $^3J_{HH}$ 4.0), 1.29–1.83 m [48H, $CH_3(C\underline{H}_2)_7$], 3.32 d (2H, PCH_2N, $^2J_{HP}$ 4.0), 3.68 s (2H, NCH_2COO), 7.37 m (Ar). ^{13}C–{H} NMR spectrum ($CDCl_3$), δ, ppm: 14.04 (CH_3), 21.60 ($\underline{C}H_2CH_2CH_2P$), 22.60 ($CH_3\underline{C}H_2$), 26.61 ($P\underline{C}H_2CH_2$, $^1J_{CP}$ 64.0 Hz), 29.09 ($CH_3CH_2CH_2\underline{C}H_2$ + $CH_3CH_2CH_2CH_2\underline{C}H_2$), 31.23 d ($PCH_2\underline{C}H_2$, $^2J_{CP}$ 13.0), 31.77 ($CH_3CH_2\underline{C}H_2$), 53.6 d (PCH_2N, $^1J_{CP}$ 79.0 Hz), 58.04 ($N\underline{C}H_2COO$), 172.22 (COOH). ^{31}P–{H} NMR spectrum ($CDCl_3$): δ_P 50.30 ppm. Mass spectrum (ESI-HRMS): *m*/*z* 670.5066 $[M + Na]^+$ (calculated: 670.5069). Found, %: C 66.79; H 11.78; O 9.76; N 2.05; P 9.62. $C_{36}H_{75}NO_4P_2$. Calculated, %: C 66.73; H 11.67; O 9.88; N 2.16; P 9.56.

NMR spectra were recorded using a Bruker AVANCE III HD NanoBay spectrometer at 400 (^{1}H), 100 (^{13}C), or 121.4 (^{31}P) MHz. Mass spectra were registered using an AB Sciex 5600 high-resolution mass spectrometer under positive electrospray ionization (ionization source DuoSpray, probe TIS, voltage 5500 V) in the TOF MS mode.

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