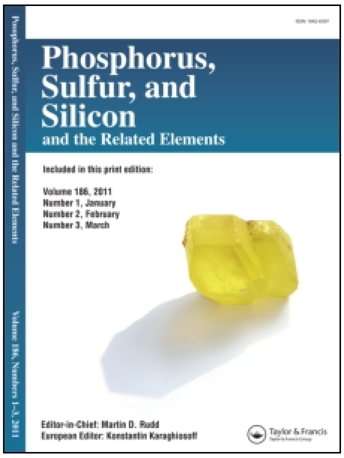

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Functionalized Phosphoryl Compounds: Synthesis, Extraction, Transport and Ionophore Properties

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Functionalized Phosphoryl Compounds: Synthesis, Extraction, Transport and Ionophore Properties

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The row of phosphoryl compounds, having additional functional groups with complexating abilities were synthesized via the classical methods of the organophosphorus chemistry. The extraction properties of the mono- and biphosphorilated amines were investigated and it is shown the high efficiency and selectivity of the noble metal ions extraction from acid water solutions. Some phosphorylated azapodands were obtained by Kabachnik–Fields reaction and their membrane transport and ionophoric properties were investigated.

Keywords Aminophosphonates; extraction; interphase distribution; ion-selective electrodes; membrane transport; phosphorylated azapodands; phosphoryl compounds

INTRODUCTION

The neutral organic oxygen, nitrogen and phosphorus derivatives have the well-defined complexating abilities. The high-efficient extractants of the metals' ions, organic and mineral acids and other substrates as well as membrane-transport and the ionophoric reactants are designed on the base of these compounds. The appearance of the electron-donating groups in one molecule doesn't lead to simple summarizing or to combination of their practically useful properties but can give the really new shapes to the molecules application.

Here we report the results of our investigation of the extraction, membrane-transport and ionophoric properties of the functionalized phosphoryl compounds having the electron-donating nitrogen- and oxygen-containing potential coordination centers in

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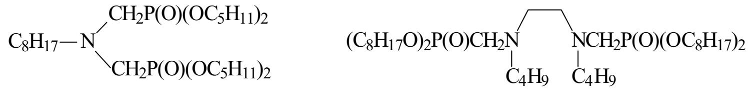
the α- and β-positions towards the phosphorus atom. The target α-aminophosphoryl compounds (α-Af) were synthesized by Kabachnik–Fields and Pudovik reactions.[1] The β-aminophosphonates (β-Af) are obtained via the phosphonethylation reaction.[2] The alkyl- and oxyalkylphosphonates are synthesized by Michaelis-Bekker reaction. The hydroxymethyl-derivatives of the four-coordinated phosphorus are obtained via the formaldehyde hydrophosphorylation.[3]

The measuring of acid—basic properties of α- and β-Af's showed that they all are weaker base than their precursors—the corresponding amines. The phosphoryl group located in the α-position to the nitrogen atom causes the reduction on 4–5 units. The accepting influence of the phosphoryl substituent in the β-position is lower—here the pKa values differ only on 2–3 units.[2] We have studied the behavior of the series of the α-Af's in interphase extraction systems water—different organic solvents. There are good linear correlations between the values of distribution constant and number of carbon atoms in Af molecules.[4] Due to this matter the conclusions were made, that α-Af's, containing more then 20 carbon atoms, will be the most appropriate extractants. According to these conclusions we have chosen α-Af $[C_4H_9(C_2H_5)CHCH_2]_2P(O)CH_2N(C_4H_9)C_8H_{17}$ (1) for the extraction of noble metals. The combination of the ramified 2-ethyl-hexyl substituents by phosphorus and alkyl groups by the nitrogen atoms allows achieving necessary hydrophilic–lypophilic balance.

We have investigated the extraction of noble metal ions by the selected Af (1) from hydrochloric media. The Au(III) is extracted quantitatively at whole interval of acidity ($C_{HCl} = 0.01$–6 M) by anion—changing mechanism. The Pd(II) extraction's mechanism depends on hydrogen chloride concentration in water phase. At low concentrations ($C_{HCI} < 0.3$ M) the complex, containing two molecules of the Af, passes into organic phase. The same mechanism takes place for the Pt(IV) extraction. The increasing of the acidity ($C_{HCl} > 0.3$ M) changes the extraction process into anion-changing route. And so, Af's are suitable for the group extraction of noble metals at the low hydrogen chloride concentrations. We have also revealed the high selectivity of the noble metals separation from the coexisting Fe(III), Cu(II), Co(II) and Ni(II) ions, via the usage of the suggested Af (I) as an extractant.[5]

We have investigated the possibility of the separation of noble metals each from other by bifunctionalised Af's (2) and (3) and have shown, that they allow separating the Au(III) from Pd(II) and Pt(IV) by the extraction at the low hydrogen chloride concentration.[6]

We have compared the transport properties of the phosphoryl compounds having the extra basic hydroxy-, alkoxy- and nitrogen-containing functional groups with the different properties towards the



(2)

(3)

SCHEME 1

strong mineral one basic perchloric acid as well as with the couple of the two-basic organic acids–oxalic and tartaric acids.[3] It was shown, that the structure of the substituents near the phosphorus atom defines the flow value. The changes of the electron-donor alkyl onto the accepting alkoxy-groups dramatically decrease the flow value of perchloric acid. When we use the α-Af instead of the phosphorylated alcohols and esters we observe the drastic increasing of the perchloric acid transport effectiveness. This result can be caused to our mind with the transfer of the protonation center from the phosphoryl oxygen to the nitrogen. This effect can not be observed for the polybasic acids that can be explained with the high-hydrophility of the ion associates having the carboxyl groups that are not linked with the carrier molecule.

A new direction in the chemistry of α-Af is the creation of azapodands with terminal aminophosphoryl groups, which can form donor–acceptor complexes "guest-host" type. We worked up efficient methods their synthesis azapodandes on the base of the Kabachnik–Fields reaction [7]. We have shown that the flow values depend on the nature of substituents by the phosphorus atom and the lengths of the polyethers chain. We established too, that some of the new azapodands can be used as the component of ion–selective electrodes for the determination of the small amount of the alkali and alkali-earth metal ions, as well as perchlorate and iodine-anions.[8]

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