# Brief Communications

## Membrane separation of ions for the preparation of pure solutions of heteropolycompounds

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Reverse osmosis was used for the separation of various types of heteropolyanions (HPA): $[PW_{11}O_{39}M(H_2O)]^{k-}$ (M = $Co^{II}$, $Fe^{III}$, $Cr^{III}$), $[(PW_{11}O_{39}Fe)_2O]^{10-}$, and $[PW_{11}O_{39}\cdot Fe_nO_xH_y]^{p-}$ from contaminant ions $NO_3^-$ and $Na^+$ that are usually introduced into the solution in the synthesis of HPA.

**Key words:** membrane separation, heteropolycompounds, nitrate ions.

When heteropolycompounds (HPC) are used as homogeneous and, especially, heterogeneous catalysts, the problem arises of separating the HPC from other ions that are introduced into the solution in the synthesis. Keggin-type HPC containing various transition-metal ions are usually obtained by the interaction of so-called unsaturated HPC with the metal salts,[1] for example:

$$Na_7PW_{11}O_{39} + Fe(NO_3)_3 \longrightarrow Na_4PW_{11}O_{39}Fe(H_2O) + 3NaNO_3. \qquad (1)$$

Conventional purification methods by extraction of HPC with ether from acidic solutions or by decomposition of nitrate on calcining the solids cannot be used, because they result in the decomposition of the HPC. Reverse osmosis using the composite membranes has been suggested[2] to separate $NO_3^-$ ions from the heteropolyanion (HPA) of the formula $PW_{11}O_{39}Fe(H_2O)^{4-}$. Here we have extended this procedure to other M-substituted HPC with Keggin's framework that are obtained according to a reaction similar to (1) and also to polynuclear hydroxocomplexes supported onto the heteropolyanion[3] and synthesized according to the equation

$$Na_7PW_{11}O_{39} + 4Fe(NO_3)_3 + 4.8Na_2CO_3 \longrightarrow Na_{4.6}PW_{11}O_{39}\cdot Fe_4O_xH_y + 12NaNO_3 + CO_2\uparrow. \qquad (2)$$

The selectivity with respect to the HPC was the same as in earlier examples[2] and was as high as 99.5 %. Since the selectivity with respect to $NO_3^-$ ions is much lower (~60 %), the relative concentration of $NO_3^-$ ions in a nonpermeate decreases. Determination of the residual concentration of nitrate ions in nonpermeates has shown (Table 1) that two or three cycles of purification are sufficient to remove 80—90 % of the initial amount of $NO_3^-$ ions from the original solutions of HPC. For HPC **4**, $NO_3^-$ ions were not detected in a nonpermeate after three purification cycles. Total losses in Co, Fe, Cr in nonpermeates were in the range of 1—1.5 %.

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**Table 1.** Composition of the HPC solutions following membrane treatment

| HPC | $N$ | pH | | $[NO_3^-]_{n/p}$ | $[M]_{n/p}$ | $[Na]_{n/p}$ | HPC composition, averaged |
|---|---|---|---|---|---|---|---|
| | | init. | fin. | mol L$^{-1}$ | | | |
| **1** | 2 | 2.15 | 2.25 | 0.06 | 0.223 | 0.760 | $Na_{3.1}H_{0.9}PW_{11}Fe(H_2O)O_{39}$ |
| **2** | 3 | 4.5 | 5.0 | 0.05 | 0.224 | 0.860 | $Na_{3.6}H_{1.4}PW_{11}Co(H_2O)O_{39}$ |
| **3** | 2 | 2.8 | 2.3 | 0.03 | 0.282 | 0.842 | $Na_3HPW_{11}Cr(H_2O)O_{39}$ |
| **4** | 3 | 3.7 | 3.95 | 0 | 0.370 | 0.470 | $Na_{5.1}PW_{11}O_{39} \cdot Fe_4O_xH_y$ |

*Note.* $[HPC]_{init}$ = 0.22 mol L$^{-1}$ (**1**—**3**), 0.05 mol L$^{-1}$ (**4**). $N$ is the number of cycles, n/p — nonpermeate.

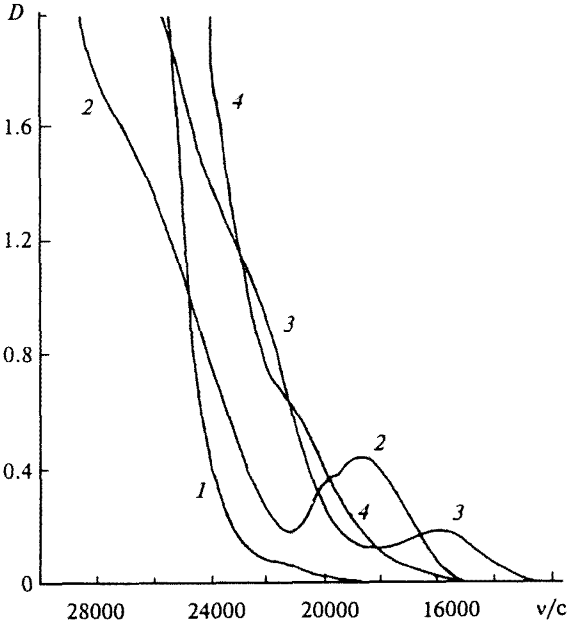

**Fig. 1.** Absorption spectra of HPC solutions following membrane treatment:
*1*, 0.22 mol L$^{-1}$ $Na_{3.1}H_{0.9}PW_{11}Fe(H_2O)O_{39}$ ($l$ = 0.207 mm);
*2*, 0.22 mol L$^{-1}$ $Na_{3.6}H_{1.4}PW_{11}Co(H_2O)O_{39}$ ($l$ = 0.207 mm);
*3*, 0.28 mol L$^{-1}$ $Na_3HPW_{11}Cr(H_2O)O_{39}$ ($l$ = 0.207 mm);
*4*, 0.092 mol L$^{-1}$ $Na_{5.1}PW_{11}O_{39} \cdot Fe_4O_xH_y$ ($l$ = 0.06 mm).

The change in the pH of the solutions due to the concentration of the HPC and removal of $NaNO_3$ upon membrane treatment is low (see Table 1) and is within the limits of HPC stability. Identity of the absorption spectra for the initial solutions with those for nonpermeates (Fig. 1) and elemental analysis confirm that the HPC composition remains unchanged upon membrane treatment.

The main amount of $Na^+$ ions introduced into the solutions in the synthesis of HPC is removed in the membrane purification as $NaNO_3$. The determination of the residual sodium in nonpermeates made it possible to refine the mean composition of the HPC following removal of the extraneous (see Table 1). At a specified pH, HPC **1**—**3** exist as acid salts. HPC **4** involve *ca.* 5 $Na^+$ ions, thus corresponding to the stoichiometry of Eq. (2). $^{31}P$ NMR spectra of both the initial HPC **4** and that in the nonpermeate consist of two signals with chemical shifts (relative to external 85 % $H_3PO_4$) 46.7 ppm (55 % of total intensity) and 196.5 ppm (45 %). According to the literature data,[3] they belong to heteropolyanions $[(PW_{11}O_{39}Fe)_2O]^{10-}$ (**1**) and $[PW_{11}O_{39} \cdot Fe_8O_zH_q]^{p-}$ (**2**), respectively. If one assumes that 10 $Na^+$ ions are bound with HPA **1** then HPA **2**, according to the stoichiometry, includes 5 $Na^+$ ions. Apparently, the polynuclear hydroxofragment $[Fe_8O_zH_q]$ in heteropolyanion **2** carries a positive charge, which favors its strong binding to $PW_{11}O_{39}^{7-}$ ion.

Thus, application of reverse-osmosis membranes allows one to remove contaminant ions efficiently from heteropolycompounds involving various transition metal ions, and the composition of HPC remains unchanged.

## Experimental

For the synthesis of HPC by Eq. (1), a weighed amount of $Fe(NO_3)_3 \cdot 9H_2O$ (HPC **1**), $Co(NO_3)_2 \cdot 6H_2O$ (HPC **2**), or $Cr(NO_3)_3 \cdot 9H_2O$ (HPC **3**) was added to a 0.22 $M$ solution of $Na_7PW_{11}O_{39}$ (pH 5). For HPC **4**, the synthesis was performed according to Eq. (2), and following mixing of the salts a solution of $Na_2CO_3$ was added until pH 3.7 was reached (2.9 mL of 2.07 $M$ $Na_2CO_3$ solution for 25 mL of 0.05 $M$ $Na_7PW_{11}O_{39}$ solution). The membrane separation of $NO_3^-$ ions from HPC was carried out according to the following typical operating procedure. The initial solution was diluted ~twofold, placed into a membrane cell,[2] and subjected to a baromembrane treatment. The samples of permeate were analyzed for P and W by atomic emission spectroscopy, for Fe, Co, and Cr by atomic absorption method, for Na by flame photometry, and for $NO_3^-$ ions by $^{14}N$ NMR with $NaNO_3$ as a standard. The nonpermeate was diluted again, and the cycle was repeated. The selectivity of a membrane with respect to HPC was calculated by the equation $S = 100\,\% \cdot (C_0 - C)/C_0$, where $C_0$ and $C$ are the concentrations of the compound in the initial solution and in the permeate, respectively.

NMR spectra were recorded on a Bruker MSL-400 spectrometer at 161.98 MHz ($^{31}P$) and 28.9 MHz ($^{14}N$). The chemical shifts (δ) are given relative to aqueous 85 % phosphoric acid ($^{31}P$) and $NaNO_3$ solution ($^{14}N$).

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# A free-radical reaction of alkanoic acids with tetrachloroethylene

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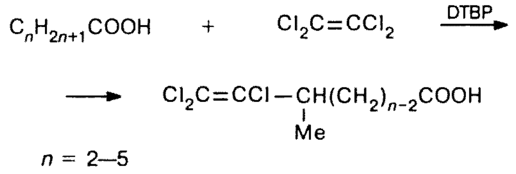
The di-*tert*-butyl peroxide-initiated free-radical reaction of $C_3$—$C_6$ alkanoic acids with tetrachloroethylene results in the formation of a mixture of isomeric (trichlorovinyl)alkanoic acids with the predominant isomer bearing the trichlorovinyl group at the (ω−1) position.

**Key words:** free radical reaction, alkanoic acids, tetrachloroethylene, (trichlorovinyl)alkanoic acids.

Alkanoic acids add to alkenes *via* the radical mechanism with a high regioselectivity, and the reaction occurs at the α-C atom of the acid.[1] Esters of mono- and dialkanoic acids behave similarly: almost exclusively α-$CH_2$ groups of the acyl fragment participate in reactions with alkenes.[1] Unlike alkenes, under the action of peroxide initiators, tetrachloroethylene (TCE) reacts with esters, ethyl chloroacetate and dimethyl succinate, at the α-C—H bond of the alkoxyl fragment to form the products of substitution of the H atom for the trichlorovinyl group.[2]

In the present work, the reactions of $C_3$-, $C_4$-, $C_5$-, and $C_6$-alkanoic acids with TCE initiated by di-*tert*-butyl peroxide (DTBP) are carried out. It is established that the process occurs with the formation of 1 : 1 adducts: isomeric (trichlorovinyl)alkanoic acids (TCVA) bearing the trichlorovinyl group at various carbon atoms of the acid, but predominantly at the ω−1 position.



$$C_nH_{2n+1}COOH + Cl_2C{=}CCl_2 \xrightarrow{DTBP} Cl_2C{=}CCl{-}\underset{\displaystyle Me}{CH}(CH_2)_{n-2}COOH$$

$n$ = 2—5

In propionic and butyric acids, the hydrogen atom is substituted for the trichlorovinyl group mainly in the $CH_2$ groups and to a lesser extent in the $CH_3$ group, while in pentanoic and hexanoic acids it is substituted almost exclusively in the $CH_2$ groups. The reaction conditions and the overall preparative yield of TCVA (a mixture of isomers isolated by distillation *in vacuo*) are presented in Table 1. The proportion of (ω−1)-TCVA in the total amount of isomeric TCVA obtained from $C_3$—$C_6$-alkanoic acids is 65—70 % (Table 2).

The mechanism of the reactions of alkanoic acids with TCE is similar to that presented previously[2] for esters. The key stages are the addition of carbon-centered $C_nH_{2n}COOH\rceil^{\bullet}$ radicals, which originate from the acid at the initiation and chain transfer stages, to TCE followed by the elimination of the chlorine atom from the adduct-radicals formed, and the chlorine atom continues the chain process.

$$C_nH_{2n}COOH\rceil^{\bullet} + Cl_2C{=}CCl_2 \longrightarrow$$

$$\longrightarrow Cl_2\dot{C}{=}CCl_2C_nH_{2n}COOH \longrightarrow$$

$$\longrightarrow Cl_2C{=}CClC_nH_{2n}COOH + Cl^{\bullet}$$

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