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PHYSICOCHEMICAL STUDIES OF SYSTEMS AND PROCESSES

Phosphoric Acid Cation Exchanger Based on Immobilized *cis*-Calix[4]resorcinolarene

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Abstract—New phosphoric acid cation exchanger was synthesized on the basis of immobilized calix[4] resorcinolarene and its service characteristics were determined.

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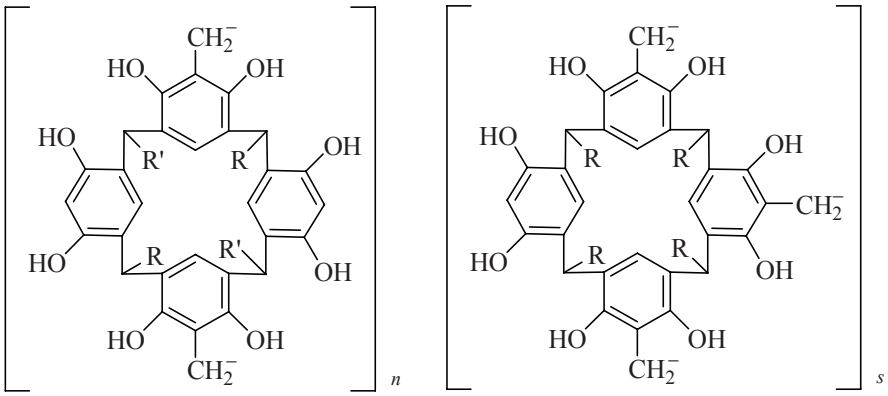
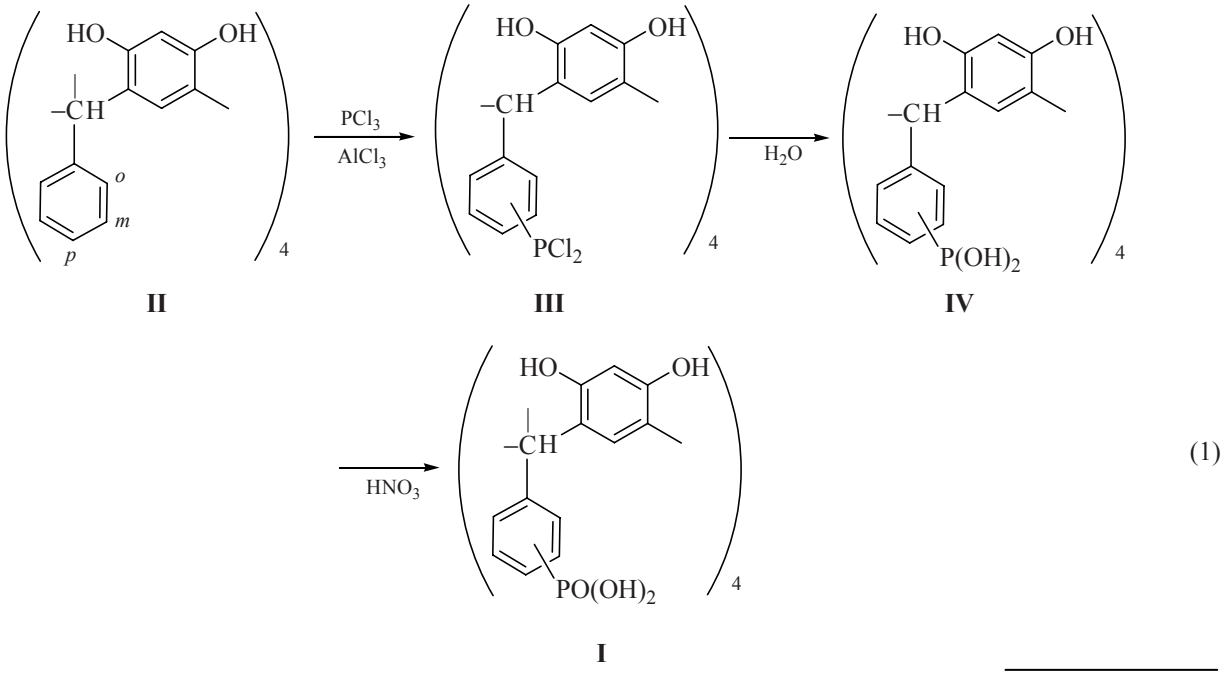
Owing to their unique structure, calixarenes are an object of keen researchers' interest [1]. It has been shown that immobilized calix[4]arenes form in the polymeric phase supramolecular ensembles involving metal cations [2–6]. Network polymers containing immobilized calix[4]resorcinolarenes have been synthesized [4, 7–9]. It has been shown that these polymers are biomimetics [4], nanoreactors for catalytic hydrogenation [10], solid polyelectrolytes [11], and weakly acidic cation exchangers [4]. The ion-exchange and ionophore properties of network polymers based on immobilized calix[4]resorcinolarenes are due to the presence of phenol (resorcinol) OH groups capable of being ionized in an alkaline medium at pH > 7. The functionalization of immobilized calixarenes by introduction into the polymer unit of carboxy [5], sulfoacid [12], and furyl(hydroxy) methyl groups [4] improves the selectivity of the ion exchange.

It is known [13] that phosphoric acid cation exchangers show selectivity toward heavy metal cations. In particular, industrial phosphoric acid cation exchangers have an increased radiation resistance and are used for sorption of indium cations from production solutions.

In the present study, a new phosphoric acid cation exchanger **I** was synthesized on the basis of immobilized *cis*-tetraphenylcalix[4]resorcinolarene. Its total dynamic ion-exchange capacity and the dynamic exchange capacity for Na^+, Tl^+, Sr^{2+}, and In^{3+} cations were determined. Below is given the hypothetic structure of the elementary unit of cation exchanger **I**:



R = Ph, R' = Ph–PO_3H_2.



II **III** **IV**

I (1)

Cation exchanger **I** was synthesized using the scheme presented below. Scheme (1) disregards the 3D structure of the polymers.

Polymer **II** and PCl_3 were condensed by the Friedel–Crafts reaction. Subsequent hydrolysis and oxidation of polymer **III** yield *cis*-tetraphenylcalix[4] resorcinolarene immobilized in the polymeric phase and functionalized with phosphonic acid groups, cation exchanger **I**.

The aim of this study was to synthesize phosphoric acid cation exchanger **I** and determine its basic ion-exchange characteristics (cation-exchange capacity, potentiometric titration curves).

EXPERIMENTAL

In accordance with scheme (1), phosphoric acid cation exchanger **I** was synthesized by several successive stages: synthesis of polymer **II**, condensation of polymer **II** and PCl_3, hydrolysis of polymer **III**, and oxidation of polymer **IV**.

Polymer **II**, calix[4]resorcinolarene immobilized in a network polymer, was obtained in the form of spherical grains by resol polycondensation of *cis*-tetraphenylcalix[4]resorcinolarene with formaldehyde [8].

For condensation of polymer **II** and PCl_3, 5 g of polymer **II** was charged into a reaction vessel, poured over with 30 ml of PCl_3, and kept at room temperature for 12 h. Then 100 ml of dichloroethane was added, the mixture was agitated for 5 h at 70°C, 3.4 g of $AlCl_3$ was added, and, without terminating the agitation, the mixture was heated for additional 10 h. Then the vigorously agitated reaction mass was poured into ice water. The resulting phosphorylated polymer **III** was separated by filtration and washed with water.

To perform hydrolysis, polymer **III** was charged into the reaction vessel, poured over with water, and placed on a boiling water bath for 1.5 h. Then water was decanted, 100 ml of 0.2 M NaOH was added, and the mixture was kept at 50°C for 3 h and washed with water to remove the alkali to a neutral reaction to give polymer **IV**.

Polymer **IV** was oxidized with 25% nitric acid at 50°C for 4 h. Washing with water yielded polymer **I**: *cis*-calix[4]resorcinolarene immobilized in the polymeric phase and functionalized with phosphonic acid groups.

The dynamic ion-exchange capacity was determined and potentiometric titration of cation exchanger **I** was performed using the procedures described in [4]. The phosphorus content of polymer samples was found by the method [15].

FTIR spectra of the samples under study were measured with a Bruker Optics TENSOR-27 Fourier spectrometer. The spectra were obtained from samples

in the form of compacted KBr pellets with a polymer under study.

Quantum-chemical calculations were made using the PM3 semi-empirical method with MOPAC 2000 software.

To consider the thermodynamic probability of an electrophilic attack on compound **II** by PCl_3, it is assumed that the process occurs by the reversible reaction

$$LH_4 + nPCl_3 \rightleftarrows LH_{4-n}(PCl_2)_n + n\text{HCl}. \quad (2)$$

The probability of occurrence of process (2) and its yield of target products depend on the composition of the reaction mixture and on the thermodynamic potential of process (2), with the latter determined by changes in enthalpy, ΔH_n^0. On the whole, the lower ΔH_n^0 for process (2), the higher its thermodynamic probability. The minimum calculated enthalpies of formation of compound **III**, $\Delta_f\Delta H_{298}^0$, and changes in the enthalpy of process (2), ΔH_n^0, are listed in Table 1. Analysis of the data in Table 1 shows that the phosphorylation process (2) must occur in the endothermic mode. In phosphorylation of *cis*-tetraphenylcalix[4] resorcinolarene at the tetraresorcinol zone, about 108 kJ of heat is absorbed per mole of $–PCl_2$. In phosphorylation of phenyl substituents at C^1 atom in polymer **II**, 54–59 kJ is absorbed per mole of $–PCl_2$.

According to the results of quantum-chemical calculations, compound **III** may contain a $–PCl_2$ group in the *m*- or *p*-position of the phenyl substituent at C^1 atom, because the position of the $–PCl_2$ group in the tetraresorcinol zone of compound **III** is energetically less favorable (it is accompanied by a pronounced positive change in the enthalpy, ΔH_n^0, Table 1). The thermodynamic probability of process (2) decreases as the number of $–PCl_2$ groups in the reaction products becomes greater. The quantum-chemical calculation demonstrated that two $–PCl_2$ groups can be introduced into diametrically opposite benzene rings of the tetraphenyl zone of macrocycle **II**. Naturally, it is necessary to elevate temperature to raise the extent of the endothermic reaction (2). No more than two $–PCl_2$ groups per macrocycle of compound **I** can be introduced in an experiment.

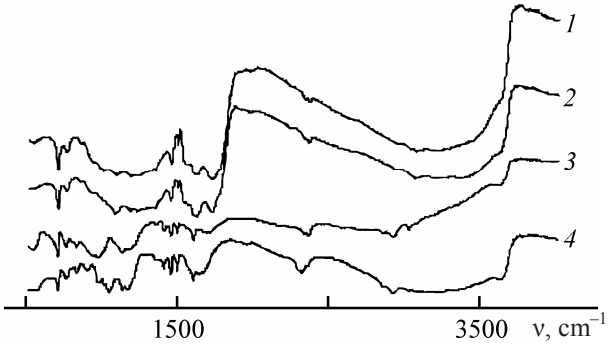


Fig. 1. FTIR spectra: cation exchanger **I** in (*1*) H-form and (*2*) Na-form; KF-1 cation exchanger in (*3*) H-form, and (*4*) Na-form. (ν) Wave number.

The FTIR absorption spectra of the polymers are shown in Fig. 1. The spectra of polymer **I** in H- and Na-forms contain broad bands at 3340 and 3170 cm^{-1}, associated with vibrations of intramolecular hydrogen

Table 1. Enthalpies of formation ($\Delta_f H_{298}^0$), changes in the enthalpies of process (2) (ΔH_n^0), and changes in the enthalpies of separate stages of process (2) ($\Delta\Delta H_n^0 = \Delta H_n^0 - \Delta H_{n-1}^0$), calculated by the PM3 method: $\Delta_f H_{298}^0(PCl_3) = –428.2$ kJ mol^{-1}, $\Delta_f H_{298}^0(HCl) = –99.1$ kJ mol^{-1}

Compound	*n*	$\Delta_f H_{298}^0$, kJ mol^{-1}	ΔH_n^0, kJ mol^{-1}	$\Delta\Delta H_n^0$, kJ mol^{-1}
Phosphorylation of the aromatic rings of the upper (tetraresorcinol) zone of *cis*-tetraphenylcalix[4]resorcinolarene **II**				
LH_4		–629.7		
$LH_3{\cdot}PCl_2$	1	–949.3	108.3	108.3
Phosphorylation of the phenyl substituents at C^1 atom of *cis*-tetraphenylcalix[4]resorcinolarene **II**				
LH_4		–629.7		
$LH_3{\cdot}PCl_2$	1	–998.7	58.9	58.9
$LH_2{\cdot}(PCl_2)_2$	2	–1272.2	114.7	55.8
$LH{\cdot}(PCl_2)_3$	3	–1547.5	168.4	53.8
$L{\cdot}(PCl_2)_4$	4	–1819.9	225.1	56.8

Table 2. Characteristics of the phosphoric acid cation exchanger based on immobilized *cis*-tetraphenylcalix[4]resorcinolarene

Characteristic	Description, value
Outward appearance	Light brown spherical grains
Functional groups	$-PO(OH)_2$, phenol OH groups
Phosphorus content, %:	
calculated	3.6
elemental analysis data	3.4
Total dynamic ion-exchange capacity for 0.1 N NaOH, mg-equiv g^{-1}	6.0±0.2
Dynamic exchange capacity, mg-equiv g^{-1}:	
for 0.1 N NaCl	1.4±0.1
for 0.1 N $TlNO_3$	1.4±0.1
for 0.1 N $SrCl_2$	1.4±0.1
for 0.1 N $InCl_3$	1.2±0.1
Ion-exchange capacity found from potentiometric titration data, mg-equiv g^{-1}	
for strongly acidic groups (pH ≤ 3.5)	1.4
total capacity	6.5

bonds in diols. The band at 3050 cm^{-1} and the doublet at 3020 and 2920 cm^{-1} are due to asymmetric and symmetric stretching vibrations of C–H bonds of the methyl-methylene groups attached to the benzene ring. The strong band at 1596 cm^{-1} is associated with stretching vibrations of C=C bonds in the benzene ring. The band observed at 1444 cm^{-1} is probably due to stretching vibrations of C=C bonds of the benzene ring and bending vibrations of C–H bonds of the CH_2 group. The FTIR spectrum of polytetraphenylcalix[4] resorcinolarene contains similar absorption bands: broad band at 3400–3500 cm^{-1}, doublet at 2940 and 2920 cm^{-1}, and bands at 2850 and 1600 cm^{-1} [16].

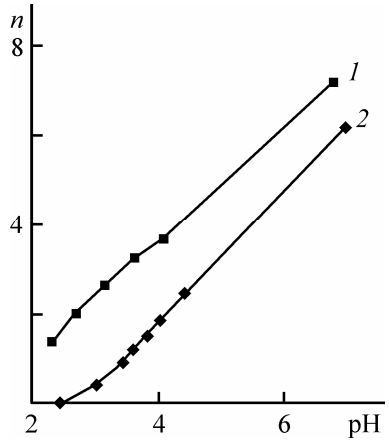


Fig. 2. Curves of potentiometric titration of cation exchanger **I** with aqueous solutions of KOH (*1*) with and (*2*) without salt additives. ($\bar{n}$) Number of cations absorbed by the cation exchanger per macrocycle of the polymer unit.

In the spectra of phosphoric acid cation exchangers in the H-form, bands appear at 920–940 and 993 cm^{-1}, which can be attributed to bending vibrations of the P–OH group. The band at 1100–1140 cm^{-1} [cation exchanger **I**] or 1200 cm^{-1} (cation exchanger KF-1) corresponds to stretching vibrations of the P=O bond. The broad band at 2330 cm^{-1} is associated with stretching vibrations of OH in $-PO(OH)_2$ groups bound by hydrogen bonds into polymeric associates.

In the spectra of phosphoric acid cation exchangers in the Na-form, bands appear at 1031 (KF-1) and 1070 cm^{-1}, attributed [17] to stretching vibrations of the $-PO_3^{2-}$ group. The bands at 920–940 and 993 cm^{-1} disappear.

The bands at 840 (polymer **I**), 815 (KF-1), 750, and 696 cm^{-1} correspond to out-of-plane bending vibrations of C–H in a disubstituted benzene ring. The FTIR spectrum of polytetraphenylcalix[4]resorcinolarene [16] contains no similar bands.

The potentiometric titration curves of polymer **I** (Fig. 2) have a shape determined by the presence of $-PO(OH)_2$ groups in the elementary unit, with one of the two hydroxyls of the $-PO(OH)_2$ group dissociating at pH ≤ 3.5.

Analysis of the material balance shows that the reaction of ion exchange from aqueous solutions involves protons of the $-PO(OH)_2$ group and four protons from the eight resorcinol OH groups (one per each resorcinol moiety) of the elementary unit of polymer **I**. Characteristics of polymer **I** are listed in Table 2.

CONCLUSIONS

(1) A new phosphoric acid cation exchanger was synthesized by condensation of a network polymer based on *cis*-tetraphenylcalix[4]resorcinolarene and PCl_3, followed by hydrolysis and oxidation of the condensation product.

(2) The cation exchanger contains phosphonic acid groups and phenol hydroxyls as ionogenic groups. The total dynamic ion-exchange capacity of the phosphoric

acid cation exchanger based on *cis*-tetraphenylcalix[4] resorcinolarene for 0.1 N NaOH is 6.0±0.2 mg-equiv g^{-1}. The dynamic exchange capacity for 0.1 N NaCl, 0.1 N $TlNO_3$, and 0.1 N $SrCl_2$ is 1.4±0.1 mg-equiv g^{-1}, and that for 0.1 N $InCl_3$, 1.2±0.1 mg-equiv g^{-1}.

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