HYBRID ORGANIC-INORGANIC NANOCOMPOSITES FOR ION-EXCHANGE PROCESSES

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ABSTRACT

Two types of composite ion-exchangers, which are based on strongly acidic gel-like cation-exchange resin and zirconium hydrophosphate, have been obtained. The first group contains both inorganic nanoparticles and their aggregates, the second one contains only aggregates. Analysis of differential porogrammes obtained with a method of standard contact porometry allowed us to estimate porous structure both of polymer matrix and inorganic constituent. Each stripe of the porogrammes has been related to structure element of polymer and ZrPh. Geometrical globular model has been applied to estimate a size of nanoparticles. A size of the nanoparticle size was shown to depend on their location: it reaches 16 nm, if the globules are placed in clusters of the polymer matrix, and 36 nm for aggregated nanoparticles in macropores. The results have been confirmed by data of scanning and transmission electron microscopy. Modification of ion-exchange resins causes transformation of porous structure of labile polymer matrix. The transformation occurs both at nano- and micro-levels. Recommendations regarding to structure of composite ion-exchangers for different applications are given.

Key words: nanocomposite, polymer matrix, zirconium hydrophosphate, cluster, channel, standard contact porometry, ion-exchanger, polymer matrix

INTRODUCTION

One of the main requirement for granulated ion-exchange resins, which are used in electromembrane processes of removal of divalent cations from solutions, is high mobility of both sorbed species and H^+ [1 - 4]. The last condition is necessary to prevent formation of insoluble hydroxide compounds in a desalination compartment of electrodialysis cell. Moreover the ion-exchangers have to provide selective removal of ionic components – this problem is actual

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since solutions to be purified usually contain Ca^{2+} and Mg^{2+} ions. Inorganic ion-exchangers are rather attractive from this point of view [2, 4]. Unfortunately the abovementioned requirements are incompatible, since electrical conductivity of inorganic materials is extremely low to provide equal rates of ion exchange and migration towards concentration compartment [2]. The problem can be solved by means of polymer modification with inorganic nanoparticles or their aggregates of micron size. Since the polymer matrix is labile, inorganic constituent is able to transform its porous structure. The aim of the work is to investigate this phenomena since the transformation probably leads to a change of functional properties of composite materials.

EXPERIMENTAL

Strong acidic gel-like cation-exchange resin Dowex HCR-S (Dow Chemical) containing approximately 8 % cross-linking agent has been chosen for investigations. The resin was impregnated with sol of hydrated zirconium dioxide or $ZrOCl_2$ solution followed by treatment with H_3PO_4 and drying of the samples at room temperature. This procedure was repeated several times. Zirconium hydrophosphate (ZrPh) particles incorporated into the polymer matrix was obtained by this manner. After each cycle of modification the sample morphology was investigated with transmission and scanning electron microscopy methods. A method of standard contact porometry was also applied, the measurements were carried out using a home-made porometer (A.N. Frumkin Institute of Physical Chemistry and Electrochemistry of the RAS) [5, 6]. Water was used as a working liquid. Electrical conductivity of packed bed of fully and partially swollen H-forms of the ion-exchangers was determined from admittance spectra. Additionally sorbed electrolyte had been previously removed from the solids. Electrical conductivity of "monolithic" materials was calculated taking into consideration the conductivity of deionized water, which was used as a non-conductive medium. Kinetics of $Ni^{2+} \rightarrow H^+$ exchange was investigated with a thin layer method.

RESULTS AND DISCUSSION

Polymer ion-exchanger includes both gel phase and empties between gel fields [7]. There are nanosized clusters (*Fig. 1 a*) formed due to dipole-dipole interaction of functional groups inside gel fields. H^+ transport is realized through clusters and narrower channels between them. Sorbed ions are transported through clusters, channels and spaces between gel fields. Their transport is due to gradient of concentration and electrical potential through each particle (ion exchange) and potential gradient through the bed (electromembrane processes).

In the case of ion-exchangers obtained by deposition from the solution, both single nanoparticles (4-20 nm) and aggregates of ZrPh have been found in the polymer matrix (*Fig. 1b, c*). The nanoparticles are evidently stabilized in

clusters and channels, at the same time their aggregates (up to several microns) are placed between gal fields. Only aggregated ZrPh nanoparticles were found after deposition from sol, a size of the aggregates is within nano- and micron diapason (*Fig.2*). Nanosized aggregates are evidently placed inside clusters, at the same time the larger aggregates occupy empties between gel fields.
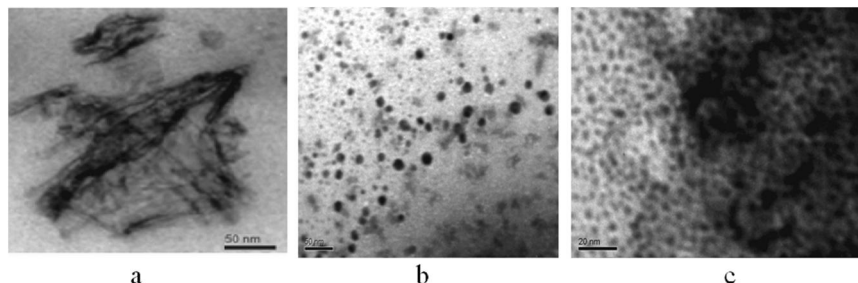

a   b   c

Fig. 1 – TEM-images of initial (a) and modified (b, c) matrix. ZrPh was deposited from a solution

Amount of the inorganic constituent in the resin was determined by a synthesis cycle (*n*). If ZrPh was deposited from a solution, first of all the empties between gel fields were filled with the aggregates ($n = 1 \div 2$), which provided increase of mass up to 35%. The aggregates act as a barrier against co-ions (Cl^-, $H_2PO_4^-$ and HPO_4^{2-}), thus uptake of excess of counter-ions (ZrO_2^+ and H^+) decreases. As a result, the aggregate formation is stopped: only non-aggregated nanoparticles are deposited in clusters and channels of gel fields ($n = 3 \div 8$). This deposition provides only a small increase of mass (up to 3%).

When ZrPh was deposited from sol, considerable increase of mass was provided during four synthesis cycles. Large pores in the aggregates provided penetration of additionally sorbed electrolyte. The aggregates play role of a barrier until encrustation of these pores.

Before porometric measurements the samples were previously vacuumized at 353 K. Removal of bonded and free water from ZrPh phase is impossible under these conditions. Thus only polymer structure has been recognized. As seen from the porogrammes (differential volume distribution, $\frac{dV}{d(\log r)}$ - log*r*, where *V* is the volume, r is the radius), porosity of the polymer matrix is much higher comparing with that for individual ZrPh (Fig. 3). Three maxima are visible in the porogramme for initial polymer. The first peak (log *r*=1(nm)) is attributed to clusters, the second one is related to spaces between gel fields (log *r*=1.4 (nm)), and the third one corresponds to structure defects of the polymer (log *r*=3.2 (nm)), which are also outside gel phase. Channel maximum (about log *r*=0 (nm) is masked with that for clusters.
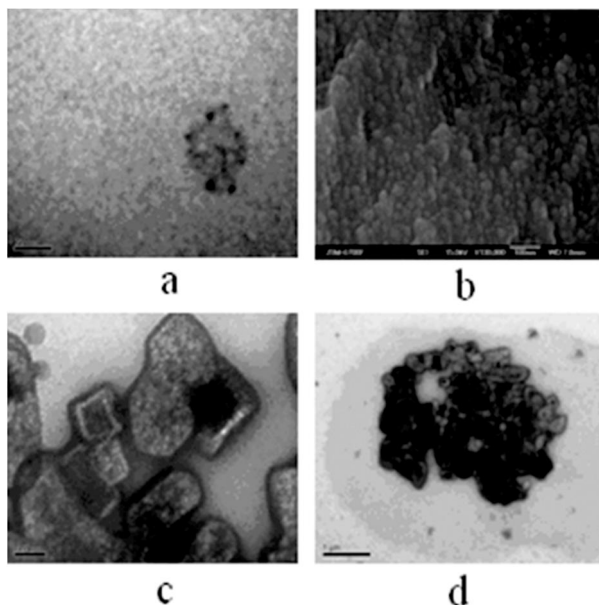
Fig. 2 – TEM (a, c, d) and SEM (b) images of modified ion-exchangers. ZrPh was deposited from a ZrO_2 sol

Insertion of the inorganic constituent into the matrix from a solution causes a decrease of mesopore volume (*Fig. 3*) probably due to corking of the cluster and channel mouths by the nanoparticles. Analysis of stripe semiwidth allows us to elucidate the influence of inorganic constituent on labile polymer matrix (*Fig. 4*). In the case of ion-exchanger obtained by means of one-time modification, the maximum attributed to clusters becomes narrower indicating their squeezing influenced by inorganic particles, which are localized outside gel phase. Widening of the maximum is caused stretching of the clusters (*n*=3), further narrowing is probably a result of screening of their surface with ZrPh nanoparticles.

Increase of macropore volume (see *Fig. 3*), which are attributed to structure defects of the polymer, is evidently due to their stretching influenced by nanoparticle aggregates. This assumption is confirmed by increase of semiwidth of the corresponding stripe (*Fig. 5*). Since no shift of the maximum at 1.6 μm has been found, the aggregates is assumed to cork spaces between gel phase. Pores inside the aggregates permit water penetration to the matrix macropores during the porometric measurements as opposed to non-aggregated nanoparticles, which form a barrier against water in clusters and channels.

In the case of composite ion-exchangers obtained from sol, both clusters and spaces between the gel fields are filled practically completely (disappearance of the maxima at log $r>10$ (nm)), however intensity of the maximum at log $r=0.2$ (nm) becomes higher indicating stretching of the channels (see *Fig.3*). Aggregates of nanoparticles in clusters are characterized by their own porous structure as opposite to single nanoparticles, the pores permit filling of channels with water during porometric measurements.
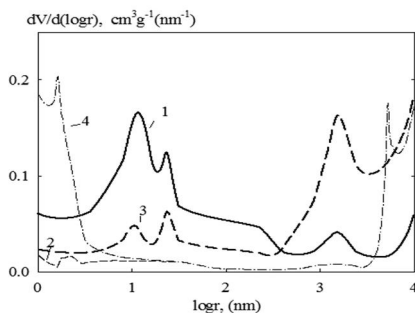
Fig. 3 – Differential pore volume distribution for initial polymer matrix (1), individual ZrPh (2), matrix modified by means of deposition from solution (3) and sol (4). Only polymer structure was recognized (1, 3, 4)
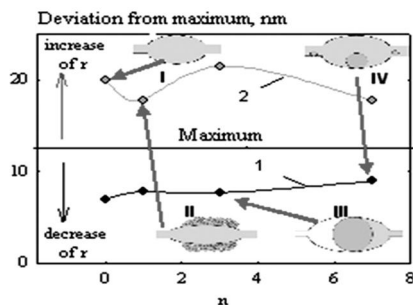
Fig. 4 – Radius value for ascending (1) and descending (2) branches of the stripes attributed to clusters, which corresponds to peak semi-height, as a function of modification cycle. The ion-exchangers contain both nanoparticles and their aggregates. Influence of inorganic constituent on clusters: I – no influence (initial polymer), II – squeezing, III – stretching, IV – screening

Treatment of the ion-exchanger with acetone before porometric measurements causes water removal from ZrPh surface, thus the porogramme shows maxima, which are typical for inorganic constituent (*Fig. 6*). Analysis of the porogramme according to globular geometrical model allows us to relate the stripes to ZrPh structure elements. Globular model gives two maxima: a peak at lower r value is attributed to narrowing of pores formed with spherical particles (pores necks) [8]. A stripe at higher r magnitudes is related to pore widening (pore cavities). Relation between radii of necks and cavities allows us to determine a type of globule packing as well as particle size. Two pairs of maxima at log r=0.2-1.2 (nm) obey globular model. The stripes at log r=0.2-0.8 (nm) give particles of 16 nm in a diameter, these particle are evidently localized in clusters (see *Fig. 2a*). These nanoparticles correspond to the first organization level. They form isolated aggregates (the second level): polymer structure makes impossible further aggregation. The peaks at log r= 0.8-1.2 nm allows us to estimate a size of particles of 36 nm. These nanoparticles (the first organization level) are placed in macropores (see *Fig. 2b*). The stripe at log r=1.5 (nm) is evidently outside the model and reflects pores between aggregates (the second level, see *Fig. 2c*). The aggregates form larger particles (the third level, see *Fig. 2d*), which are isolated from each other and cannot form pores. The peak at log r>3 (nm) evidently corresponds to structure defects inside these aggregates. Simple cubic packing has been found for the nanoparticles localized both in clusters and macropores of the polymer matrix.
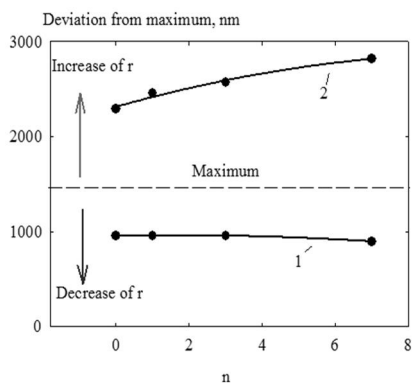
Fig. 4 – Radius value for ascending (1) and descending (2) branches of the stripes attributed to matrix macropores, which corresponds to peak semi-height, as a function of modification cycle. The ion-exchangers contain both nanoparticles and their aggregates
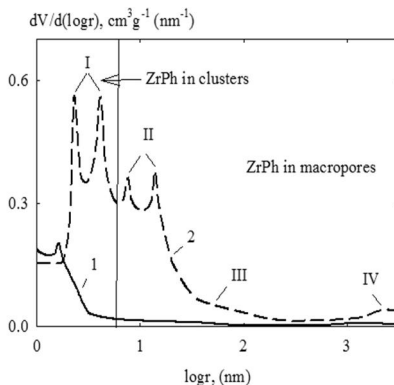

Fig. 5 – Differential distribution of pore volume for modified matrix (1) and ZrPh (2). The ion-exchanger contain only aggregates of the nanoparticles. Pores are between: I – nanoparticles in clusters, II – nanoparticles in macropores, III – aggregates of the second level, IV – structure defects of particles of the third level

When ZrPh is inserted step by step, swelling of the polymer changes due to different ways of matrix filling. Stretching of the polymer due to inorganic constituent improves swelling (n=1-3), at the same time screening of clusters and channels with nanoparticles causes a decrease of swelling (n=4-8, *Fig. 6*). Total exchange capacity per volume unit changes in opposite direction.

Electrical conductivity ($\overline{\kappa}$) of swollen samples is due to protons of functional groups localized in clusters and channels. The $\overline{\kappa}-n$ plots demonstrate both maximum and minimum (*Fig. 7*). Before the minimum a change of conductivity is caused by stretching of clusters (or both clusters and channels) and their corking by nanoparticles or their aggregates. As a result of stretching, the concentration of charge carriers per volume unit decreases on the one hand and their mobility increases on the other hand. Thus squeezing and stretching of the clusters are in a competition. After the minimum the stretching is stopped, increase in conductivity is determined only by charge carrier concentration. The screening effect is more pronounced for the samples containing both nanoparticles and their aggregates. The minimum of the $\overline{\kappa}-n$ dependence is shifted towards higher ZrPh content for the samples containing only aggregates comparing with those filled with both aggregates and single nanoparticles.
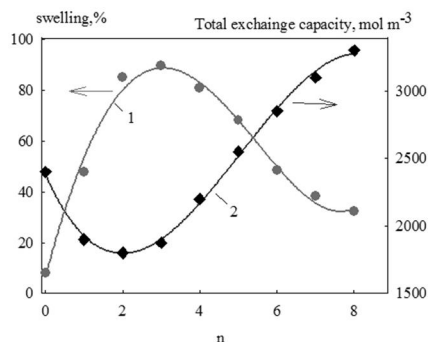
Fig. 6 – Swelling (1) and total exchange capacity (2) as functions of a number of modification cycle. The ion-exchangers contain both nanoparticles and their aggregates
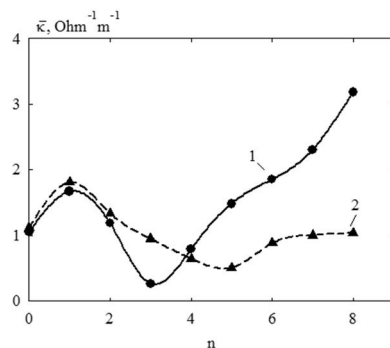

Fig. 7 – Electrical conductivity as a function of a number of modification cycle. The samples contain both nanoparticles and their aggregates (1), only aggregates (2)

Dependence of electrical conductivity on charge carrier concentration (C_H) shows two fields: the first one corresponds to modification cycles of 1-3 (*Fig. 8*). Intersection of the plots with absciss axe gives $C_H \gg 0$ mol m^{-3} at $\overline{\kappa}$ =0 Ohm^{-1}m^{-1} indicating no contribution of the aggregates in conductivity. Self-diffusion coefficient of H$^+$ obtained for squeezed-stretched polymer has been estimated as 1.9×10^{-9} m^{2}s^{-1}. In this case the resin containing 8 % cross-linking agent behaves like flexible resins, for instance, Dowex 50WX-2. The second field of the $\overline{\kappa} - C_H$ plot is attributed to screening of clusters and channels, here the self diffusion coefficient of 4.8×10^{-10} m^{2}s^{-1} has been found.
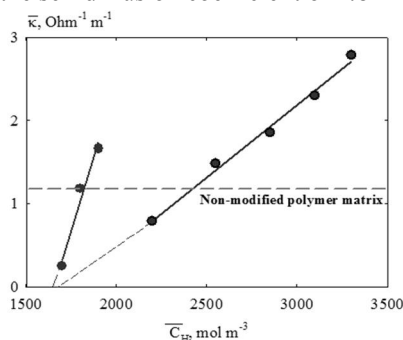

Fig. 8 – Electrical conductivity as a function of H$^+$ concentration. The ion-exchangers contain both nanoparticles and their aggregates
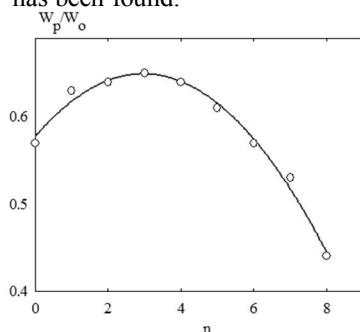

Fig. 9 – W_P/W_O ratio as a function of modification cycle. The ion-exchangers contain both nanoparticles and their aggregates

It is a normal value for the non-modified resins containing 8 % cross-linking agent. The aggregates stretch meso- and macropores, which are outside gel phase. These pores are filled with water before clusters and channels. Thus percolation threshold (W_P), which has been determined by research of partially swollen samples, increases within the interval of $n = 1$-3 (*Fig. 9*, here W_0 is the water content in completely swollen ion-exchanger).
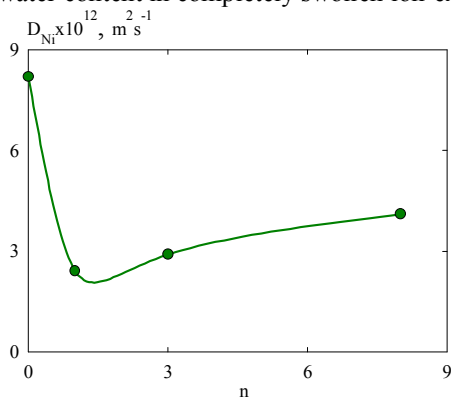

Fig. 10 – Ni^{2+} self-diffusion coefficient as a function of a number of modification cycle. The ion-exchangers contain both nanoparticles and their aggregates

Further decrease of W_P/W_O ratio is evidently due to bonded water localized on the surface of nanoparticles in clusters and channels.

During sorption process the ion transport is realized through the clusters, channels and also spaces between gel fields. Modification leads to inconsiderable decrease of Ni^{2+} self-diffusion coefficient (D_{Ni}): the order of magnitude is 10^{-12} $m^2 s^{-1}$ (*Fig. 10*). The $D_{Ni} - n$ plot shows a minimum, it is probably due to competition of Ni^{2+} interaction with functional groups of ZrPh on the one hand and stretching of the macropores on the other hand.

CONCLUSIONS

Two types of composite ion-exchangers have been obtained. The first group contains both ZrPh nanoparticles and their aggregates, the second one contains only aggregates. Analysis of differential porogrammes obtained with a method of standard contact porometry allowed us to estimate porous structure both of polymer matrix and inorganic constituent. Each stripe of the porogrammes has been related to structure element of polymer and ZrPh. Geometrical globular model was applied to estimate a size of nanoparticles. The nanoparticle size was shown to depend on their location: it reaches 16 nm, if the globules are placed in clusters of the polymer matrix, and 36 nm for nanoparticles in macropores. Two organization levels were found for the aggregates in clusters, at the same time the aggregates filling macropores show three levels. The results have been confirmed by scanning and transmission electron microscopy.

Modification of ion-exchange resins causes transformation of porous structure of labile polymer matrix. The transformation occurs both at nano- and

micro-levels. The aggregates, which are outside gel field of the matrix, squeeze clusters. The nanoparticles or their aggregates, which are placed in clusters, stretch them. The particles of inorganic constituent, which are inserted after filling of empties between gel fields, screen surface of clusters and channels.

Increase of H^+ mobility for the ion-exchangers with a minimal content of nanoparticles ($n=1÷2$) as well as small decrease of Ni^{2+} self-diffusion coefficient shows that these samples can be applied to electromembrane processes. In this case H^+ transport will be able to prevent formation of insoluble compounds inside desalination compartment of electrodialysis cell. If hybrid-organic inorganic ion-exchangers (proton-conductive membranes) are applied to fuel cells, they must be free from aggregates, since the large particles causes stretching of polymer. The stretching leads to a decrease of charge carrier concentration per volume unit and, as a result, a decrease of electric conductivity. Moreover high porosity of the aggregates causes increase of percolation threshold. Liquid crossover through these membranes is assumed to be higher comparing with that through non-modified materials.

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