

Nano Ion Exchangers as Modifiers of Chromatographic Phases and Sources of Analytical Signal

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Abstract—A method is developed for preparing of nanosized ion exchangers (nano ion exchangers, **NIEX**) as water-stable sols of a given ionic form of two types: nano cation exchangers and nano anion exchangers. According to their physicochemical properties, nano ion exchangers are simultaneously dissolved hypercharged ions and microscopic solid ion exchangers capable of solid-phase ion exchange. In chromatographic and other methods of analysis, can serve as modifiers of stationary and mobile phases, providing a high capacity of the first one and special buffer properties of the second one. Some results of using for the creation of polymodal phases for ion chromatography, as a modifier in capillary electrophoresis, and in a luminescence method for the determination of heavy metals (using copper as an example) in aqueous solutions are presented.

Keywords: nanosized polymer ion exchangers, solid-phase ion exchange, ion chromatography, capillary electrophoresis, luminescence

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The properties of particles of ion exchange resins of the nanometer range have so far almost not been studied. This is due to the complexity of the synthesis of functionalized nanopolymers, the complexity of working with them, and the lack of tasks for their application. Meanwhile, these substances are interesting not only for their high kinetic properties, but also because of the formation very stable sols and a combination of the properties of hypercharged ions and solid ion exchangers. Unlike conventional resins, nano ion exchangers can pass through macroporous membranes and filter materials, and the presence of a high charge at a small mass ensures the control of their movement and distribution at the phase boundaries. The most interesting are specific nanochemical properties of NIEX, combining the properties of solid sorbents and hypercharged polymeric ions.

Attempts to synthesize functionalized polymers based on a copolymer of styrene and divinylbenzene of nanometer size are known [1]. Synthesis of particles of ungrafted copolymer with dimensions of several tens of nanometers was successful; however, when modified to obtain a sulfonic cation exchanger or a highly basic anion exchange resin, the particles dissolved. Similar studies [2] ensures the estimation of the size of a critical nucleus in the synthesis of ion exchangers of about 60–80 nm. If we consider the problem of obtaining nano ion exchangers on the other hand, by grinding a large fraction of the prepared ion exchange-

ers, then the question arises: how to do this using abrasive surfaces of micron roughness? A doubt in the existence of NIEX occurs, i.e., in a possibility of obtaining particles with sizes smaller than the critical nucleus in the synthesis and smaller than the irregularities of the abrasive surface in grinding.

However, the solution of the problem lies both in the way to improving the synthesis and grinding of the material with the required chemical properties: for this, instead of abrasion, it is necessary to use grinding in a ball mill. In the latter case, the fragments formed when a ball strikes a particle of several microns in size may be tens and hundreds of times smaller, in particular, they may fall into the nanometer range. This method for obtaining nano ion exchangers was used in our research [3].

For ion chromatography, microparticles of ion exchangers with a size of about 10 μm, as well as particles of submicron sizes, are used as modifiers of the solid phase (see, e.g., [4]). Examples of the use of smaller particles in analytical chemistry were not found in the literature until recently.

This paper deals with the study of the use of a new class of materials, nanosized ion exchangers in analytical chemistry.

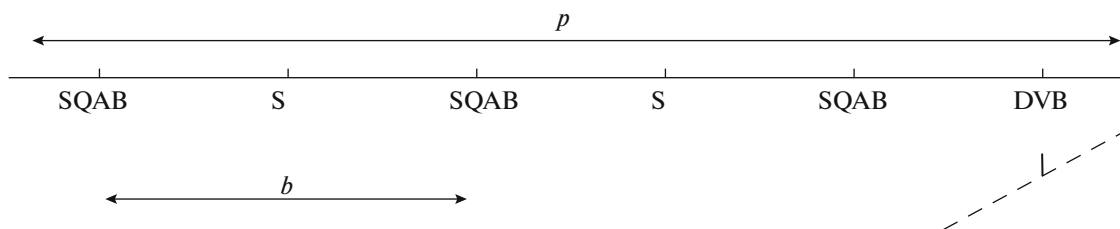


Fig. 1. Model of AV-17 polymer with the concentration of crosslinking agent (divinylbenzene) 8%. Designations are given in the text.

THEORETICAL

Structure of nano ion exchangers. The structure of a polymeric ion exchangers in general is a three-dimensional network, in nodes of which are formed by molecules of a crosslinking agent, and functional groups—fixed ions—are evenly distributed over the chains. The section of a polymer chain between two adjacent nodes is the period of the network. The period of the polymer AV-17 anionic resin with a cross-link of 8% corresponds to the fragment shown in Fig. 1. The following designations were introduced: **S** is styrene, **SQAB** is styrene with a quaternary ammonium base, and **DVB** is divinylbenzene; the dotted line denotes another polymer chain associated with that considered through DVB; the distance between the functional groups (b) and the period size of the polymer (p) are indicated. The molar mass of the fragment shown in Fig. 1 minus half the mass of the DVB 130/2 Da, belonging to another fragment and indicated by the dotted line, is $M_p = 759$ Da. The ratio of these values gives the correct value of the degree of cross-linking, 8.6%. The size of the chain section between the two functional groups is $b \approx 1.0$ nm. The size of the DVB radical is approximately $b/2$. The average radius of the cross section of a link is estimated as the van der Waals radius of the carbon atom: $t \approx 0.34$ nm.

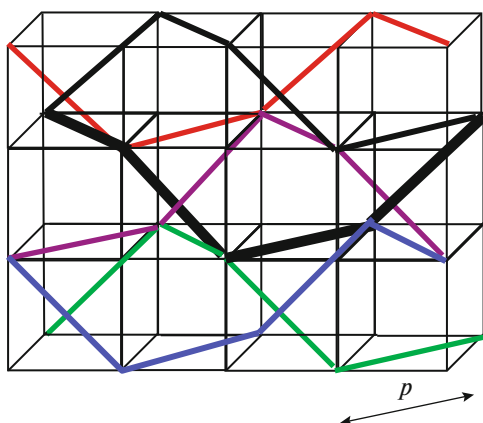


Fig. 2. A variant of placing polymer network in a cubic lattice.

The length of the period p is composed of three identical segments of length b arranged at tetrahedral angles to each other. Only two conformations are possible [5]. The longest conformation is *trans*-zigzag, for which we find $p_N = b\sqrt{19/3} \approx 2.52b \approx 2.5$ nm. The length of the *gauche*-conformation is substantially shorter: $p_V = b\sqrt{11/3} \approx 1.91b \approx 1.9$ nm. In a good solvent, which is water, the ion exchanger chain is the most straightened with $p \approx p_N$.

The polymer can be represented embedded in a cubic lattice. In principle, this possibility is confirmed by the correct estimate of the maximum change in the volume of a cross-linked polymer. The cube of the ratio of lattice periods obtained for the cases of *trans*- and *gauche*-conformations of the polymer period is 2.3, which corresponds to the limiting swelling of the ion exchanger with 8% crosslinking. The three-dimensional network of the polymer can be placed in a cubic lattice along non-intersecting diagonals of the faces, e.g., as shown in Fig. 2.

As at the nodes of this network DVB connects two tangent polymer chains, the degree of the node is 4. The network in Fig. 2 satisfies this condition: each nodal point is a tangency point of two linear chains. The links of each chain are articulated at an angle of 120° . The difference in valence angles from tetrahedral (110°) should result in the stresses in the chain and, correspondingly, in the lattice deformation. The less energetically significant torsion angles between chain links are 70.5° instead of 60° . However, it should be borne in mind that the DVB molecule is represented by a dot in the model. Taking into account its sizes and angular degrees of freedom results in a possibility of creating a weakly stressed conformation with almost regular bond and dihedral angles. In the case of point crosslinking, the diagonal of the face equals p , the lattice spacing is $p/\sqrt{2}$. The size of DVB, $b/2$, serves as an additive to the lattice spacing: $p/\sqrt{2} + b/2 \approx 2.25$ nm.

One can see in Fig. 2 that the repeating element of a tetrahedral polymer network laid in a cubic lattice contains 4 links of length p and is placed in a cube with a side in 4 lattice steps. This size (9 nm) that can be considered the minimum size of a cubic resin particle,

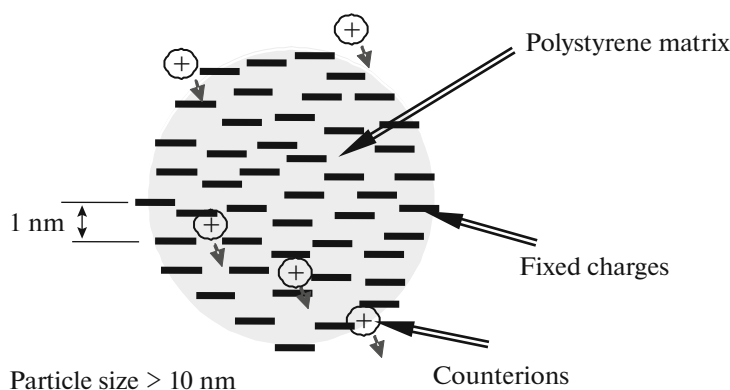


Fig. 3. Ion exchanger with an uncompensated charge of the same sign as that of fixed groups because of the dissociation of counterions.

and the minimum diameter of a spherical particle 13–15 nm. Checking these parameters in calculating the density of the polymer will give 2 g/cm³, which is acceptable, as it is less than twice the real value. The found minimum sizes characterize a critical nucleus of a solid phase only if the particle is obtained as a fragment of an already prepared network. If the particle is obtained by emulsion polymerization, the uneven radial distribution inside the drop of emulsion of the components of the mixture of monomers with different surface activities violates their proportions that are important in the synthesis. In particular, the surface layers will be enriched with water-soluble components and depleted in a crosslinking agent. Such splitting reaches tens of nanometers and, therefore, the critical nucleus will have much larger sizes, at least 60 nm according to our estimates.

Relative surface charge of the ion exchanger. The sizes of NIEIX in the range of 10–100 nm (for particles of irregular shape, the upper limit is shifted to 200 nm) determine their dual nature, i.e., existence in the form of “solid ions”. It is important to distinguish between the total and real charge of the NIEIX. The total charge is equal to the total charge of functional groups of the particle. The real charge is determined by the dissociation of functional groups on the surface of the particle, which for strong acid cation exchangers and strong base anion exchangers proceeds completely. Therefore, at the phase interface, there is a spatial separation of fixed charges located on the surface of the particle and counterions that go into the solution (Fig. 3).

For example, in a cubic particle with a side of 10 nm, with an average distance between adjacent functional groups of 1 nm, the total charge is estimated at 10³ amu in the absolute value (the atomic unit is equal to the electron charge), and the real charge, equal to the total charge of the surface groups, is 600 amu, i.e., about half as much. For particles with a size of 100 nm, these values are equal to 10⁶ and 6 × 10⁴ amu, respectively. In the second case, the real

charge is only 6% of the total one. The ratio of the real to the total charge of the ion exchanger, the relative surface charge (RSC), is a quantitative parameter expressing the ionic nature of the particle. It is obvious that it is hardly worthwhile to consider particles with RSC less than 5% as ions. This border, as one can see, coincides with the size limits of the NIEIX.

So, according to the size of the RSC, the following classification of charged particles is possible (Table 1): <5% are classical ion exchangers (which include micro- and macro ion exchangers), >50% are ions, and between 5 and 50% are NIEIX. The group of micro ion exchangers isolated in classical ion exchangers by sizes refers to chromatographic stationary phases, and macro ion exchangers are used in the ion-exchange technology. Let us note that, according to the experiments presented below, the RSC of macro ion exchangers is almost independent of the size of the granules and is 0.05–0.1%.

The right boundary of the NIEIX region of existence is also explained by the stability of their hydrosols: larger particles are subjected to sedimentation. Because of the too small RSC in this area, the electrostatic repulsion of particles does not interfere with the gravitational force. At this boundary equilibrium is established between the two flows—the Brownian diffusion J_D and the sedimentation J_{sed} :

$$J_{sed} = \frac{2g\Delta\rho r^2}{9\eta} c = \frac{k_B T}{6\pi\eta r} \frac{dc}{dH} = J_D, \quad (1)$$

where g is the acceleration of gravity, $\Delta\rho$ is the difference between the densities of the polymer and water, η is dynamic viscosity, $k_B T$ is temperature in energy units, and r is radius of the particle.

The solution of Eq. (1) is expressed by the barometric formula:

$$H = \frac{3k_B T}{4\pi r^3 g \Delta\rho}, \quad (2)$$

Table 1. Classification of charged particles by relative surface charge at an average distance between fixed charges inside the ion exchanger of 1 nm

Particle/granule name	Typical dimensions, nm	RSC, %
Ion	0.1–10	50–100
Nano ion exchanger	10–200	5–50
Micro ion exchanger	200–20000	0.1–5
Macro ion exchanger	>20000	<0.1

where $H = \text{const}$ is the height of the suspension column at which the concentration of particles c drops by a factor of e (in the direction from low to up). For ion exchangers with an internal porosity of about 50% and at a real polymer density of 1.2 g/cm^3 , we have a difference $\Delta\rho \approx 1.0 \text{ g/cm}^3$. The region of concentrations of hydrosol interesting to us covers the range from 10^{-5} to 1 M (by functional groups). The height of the column of solutions containing NIEX in our experiments does not exceed 10 cm. In accordance with Eq. (2) and taking into account the estimates made for the right boundary of the sizes of the NIEX, we obtain $r \approx 50$ nm. This estimate corresponds to a diameter of 100 nm for spherical particles. For particles in the form of plates, the maximum size will be approximately twice as large, which is consistent with Table 1.

Kinetics and dynamics of ion exchange with the participation of nano ion exchangers. Because of the relatively large mass, the diffusion mobility of nanoparticles is much lower than that of ordinary molecules or ions. In this regard, in the process of the sorption of NIEX by a macro ion exchanger of opposite polarity, convective mass transfer of nanoparticles, which strongly depends on the temperature gradient and the vortex motion of the liquid phase, comes to the fore.

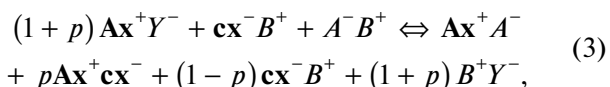
Another process associated with the exchange of the ionic forms of NIEX and macro ion exchanger of the same polarity largely involves internal diffusion. In this NIEX particle plays the role of a co-ion; therefore, the characteristic period of reaching an equilibrium in such a system includes the sum of the diffusion times inside the macro ion exchanger and inside the NIEX. The latter value is estimated in the region of dozens of milliseconds, which is much lower than the first value. The process of the exchange of ionic forms is characterized by an increased external diffusion region in view of the strong repulsion of the NIEX from the surface of the same polarity at a low ionic strength of the solution.

Let us consider an important task for the chemistry of nano ion exchangers: NIEX hydrosol, which is in solution of arbitrary composition, needs to be converted into a sol with any prescribed ionic form in a corresponding solution or in pure water. Its solution is

illustrated by the following theoretical scheme. We have introduced letter designations for ion exchangers, where the second letter is x (from “exchanger”), and the first letter is a or c corresponds to an anionic or a cationic resin, and capital letters to designate macro ion exchangers, and lower case letters, to designate nano ion exchangers.

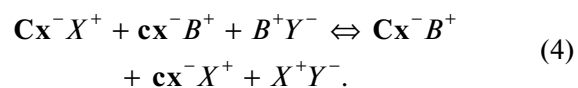
Let, for definiteness, nanocationite (NIC) is given in the form of $B(\text{cx}^-B^+)$ in equilibrium with a solution of salt AB . It is required to obtain NIC in the form of X^+ in equilibrium with a solution XY . We will carry out the following dynamic processes:

- exchange of co-ions A^- on anion-exchange column Ax^+ in the form of Y^- :



where p is the relative surface charge of the macro ion exchanger;

- exchange of counterions B^+ on the cation exchange column Cx^- in the form X^+ :



Thus, the method gives proportion $1-p$ of the target product cx^-X^+ in the XY solution with a slightly increased concentration – by $1+p$ times.

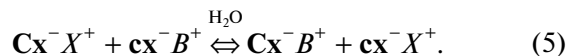
Reaction (3) proceeds in a system with two solid phases and a common liquid phase. The product of the interaction of solid phases is nanocomposite Ax^+cx^- , in which the surface of a macro ion exchanger is not blocked, providing all its volume for the exchange of counterions.

Retention of nano ion exchangers. There are two mechanisms for the retention of NIEX particles: electrostatic, due to the attraction of oppositely charged surfaces, and adsorption-mechanical, due to placing a “guest” nanoparticle in a potential well of van der Waals forces inside a macropore on the “host” surface. The first case is described above as the retention of nano ion exchangers on columns of macro ion exchangers of opposite polarity. It is described by the parameter p in Eq. (3). The second mechanism is implemented when macroporous adsorbents with pores larger than the diameter of nanoparticles are used.

Solid phase ion exchange. Attempts to observe and study solid-phase ion exchange for systems with macro ion exchangers were previously hampered by a very low speed. In systems with nano ion exchangers, the kinetics of the solid-phase ion exchange is characterized by times significantly less than 1 s, because of which it can be carried out in the usual mode for dynamic sorption experiments. In such systems, solid-phase ion exchange occurs between the macro ion

exchanger filling the column and the NIEX solution of the same polarity.

Reaction (4) in the absence of an electrolyte is written as:



It is unusual, as it involves the direct exchange of ionic forms between two solid phases. The possibility of such a process results from two model representations:

- if a particle of NIEX is presented as a co-ion, then reaction (5) will be an ordinary ion exchange reaction;
- if macro- and nanoparticles are combined within a single macro resin particle, then reaction (5) will describe the process of internal diffusion.

The difference from model systems is in kinetics: in a real system, exchange takes place slower. When comparing the second model with the first one, we found that diffusion is added inside the NIEX. In addition, the average distance between macro- and nanoparticles in a real system is larger than in the second model. It is obvious that the real systems will approach the indicated models with a decrease in the size of nanoparticles and with an increase in their concentration.

A special case of reaction (3) describes the interaction of the hydroxyl form of the macro ion exchanger $\text{Y}^- = \text{OH}^-$ with the hydrogen form of the NIEX in water:



The product of this reaction, nanocomposite $\text{Ax}^+ \text{cx}^-$, is a bipolar sorbent with a thin cation exchange layer, which can serve as a highly efficient phase in chromatography. For reaction (6), a high equilibrium constant is characteristic not only because a stable nanocomposite is formed, but also because water is one of its products.

The force of interaction in the systems macro ion exchanger–nano anion exchanger (NIA) or macro ion exchanger–NIC many times exceeds the force of interaction of a conventional ion with an ion exchanger. The system tends to the state of a nanocomposite, in which the function of the “host” is performed by the macro ion exchanger, and the role of the “guest”, by NIEX. In the “host” ion exchanger, only the outer surface and the macropores are accessible to the “guest” one. It was noted above that, for a macro ion exchanger, surface capacity is a very small proportion of the entire capacity distributed over the volume, so that the “guest” ion exchanger does not interfere with the ion exchange process on the “host” ion exchanger.

EXPERIMENTAL

In a series of experiments, sols of a KU-2 × 8 sulfonic cation exchanger of reagent grade (Russia) and a strong base AV-17 × 8 anion exchanger of reagent grade (Russia) with a matrix of styrene and 8% divinylbenzene copolymer were obtained by grinding in a ball mill and the subsequent centrifugation of aqueous suspensions. Particle sizes ranged from 50–250 nm (Fig. 4). The concentration of sols by functional groups ranged from 7 to 40 mM.

The relative concentration of the hydrosol was determined using a KFK-2 photometer (ZOMZ, Russia) using absorbance at the wavelength 315 nm.

The electrical conductivity and composition of ionic mixtures were determined using a Tsvet-3006 ion chromatograph (DOKBA, Russia), equipped with cationic and anionic two-column systems and a conductometric detector.

The luminescence experiments were carried out using a Fluorat-M fluorimeter (LUMEX, Russia) with a slit width of 10 nm and excitation band of 272 nm.

Dynamic sorption experiments were performed using glass columns with a diameter of 4 mm loaded with 1–5 mL of macro ion exchangers. The liquid phase was supplied by a peristaltic pump. At the outlet of the column, small portions of the solution were collected and analyzed.

RESULTS AND DISCUSSION

Estimation of ζ -potential of a nano ion exchanger particle. Because of the homogeneity of the distribution of functional groups in the volume of the polymer, effective charge can be assigned to the charge/mass ratio, which is a characteristic of particle mobility, i.e., the diffusion mobility of nanoparticles is proportional to the effective charge. Based on these considerations, one can estimate the ζ -potential of a NIEX particle in a dilute aqueous solution by the ion exchange capacity a_0 (mEq/mL) and particle diameter d (nm) using the formula $\zeta \sim 10 a_0 d$ (mV) in the range of 300–1000 mV.

Estimates of electrostatic potential near the surfaces of ion exchangers are known from the literature, e.g., for neighboring groups of strong base anion exchanger located at a distance of 1 nm, a potential $\zeta \sim 250$ mV [6] was found from an experiment with a homogeneous AMX-SB membrane in the Cl-form and a highly dilute NaCl solution, and was also calculated using the modified Helmholtz-Smoluchowski equation [7].

The ζ -potential described here provides the high stability of NIEX sols, which persist for many years. The same electrostatic nature causes these stable sols

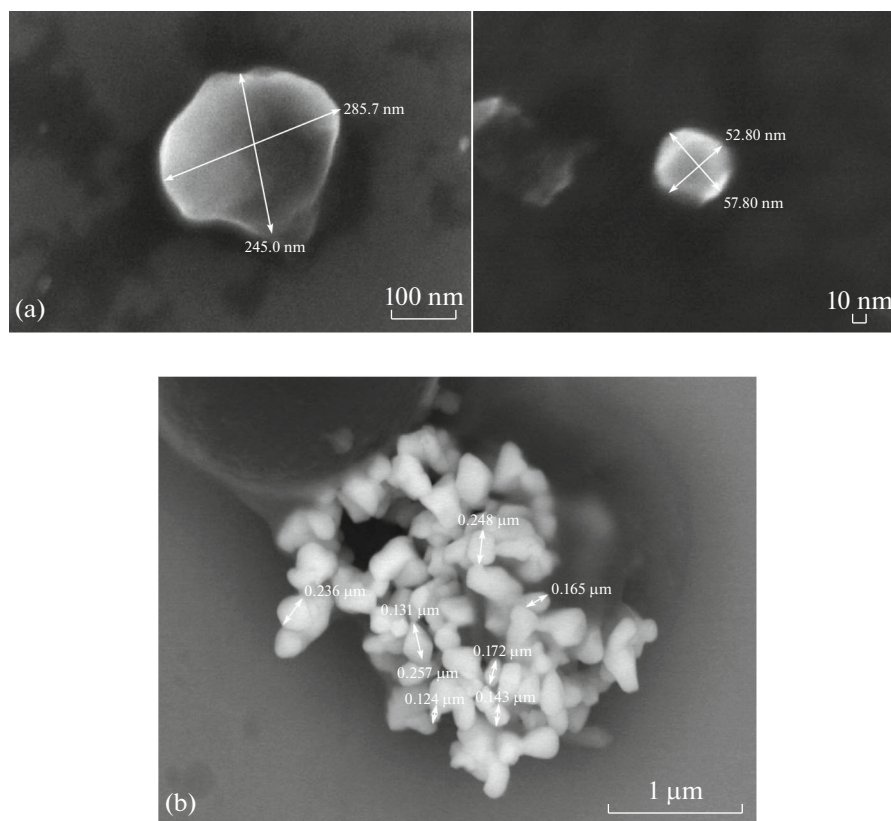


Fig. 4. Electron micrographs of particles of (a) nano cation exchanger and (b) nano anion exchanger.

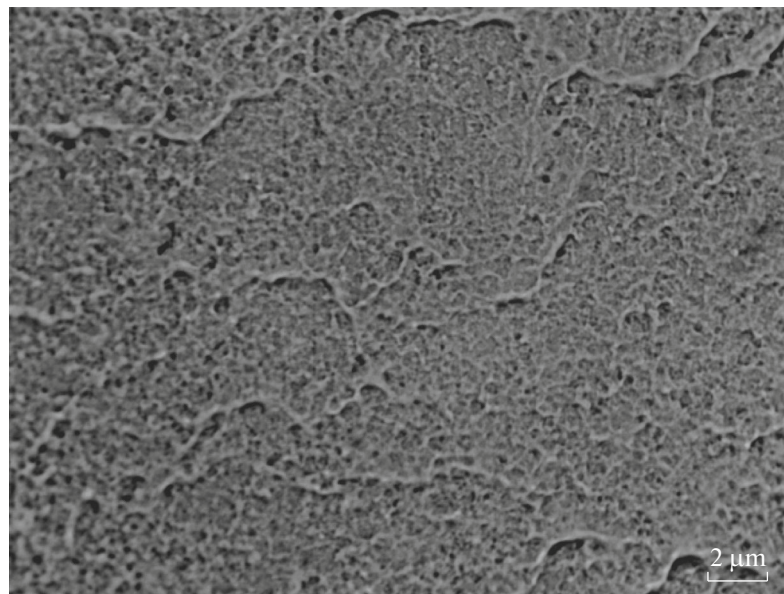


Fig. 5. Micrograph of precipitate obtained in the coagulation of heteropolar NIEX.

NIA and NIC to coagulate quickly (in seconds) when mixed. Figure 5 illustrates the dense branched structures that appear in mixing NIEX of different polarities.

The concentration of NIEX particles can be assigned to the concentration of functional groups c_{fg} through the capacity of the solid phase:

$$c_x \equiv c_{fg} = c_{sp} a_{0sp}, \quad (7)$$

where c_{sp} is the concentration of NIEX particles (g/L), a_{0sp} is the capacity of the solid phase (mol/g), i.e., density of functional groups in the polymer matrix. The value of the capacity of the solid phase can be constant for particles and known as the capacity of the initial ion exchanger for nano ion exchanger obtained by grinding. In this case, the concentration of NIEX is conveniently determined as c_x (M), if necessary, easily recalculated in c_{sp} .

Example. The sample NIC/H has a concentration of 10.7 mM by the results of titration with an alkali. The evaporation of 15 mL of hydrosol to an air-dry state gave a sediment weighing 37.9 mg, from which the mass concentration of NIC was 2.53 g/L. The ratio of the obtained values gave 4.23 mmol/g, which corresponds to the capacity of the initial KU-2-8 cationite.

Electrical conductivity and particle shape. The ratio k of electrical conductivity created by the nano ion exchanger in the form of ions I (NIEX/ I) to the electrical conductivity of solution IJ with concentration c is equal to:

$$k = \frac{c_x \lambda_{xI}}{c(\lambda_I + \lambda_J)}, \quad (8)$$

where λ_{xI} is electrical conductivity per functional group of the NIEX in the form of an ion I . Heavy NIEX particles (with a mass of the order of 10^6 Da) make a negligible contribution to electrical conductivity; therefore, its value is determined only by counterions I , the number of which is equal to the surface charge. In accordance with the definitions there is an equality:

$$\lambda_{xI} = \gamma \lambda_I, \quad (9)$$

where γ is the relative surface charge of the NIEX particle.

Combining expressions (7)–(9), we express the RSC through k :

$$\gamma = \frac{\lambda_{xI}}{\lambda_I} = k \frac{c}{c_x} \left(1 + \frac{\lambda_J}{\lambda_I} \right). \quad (10)$$

Example. In the experiment, the electrical conductivity of the sol NIC/H in water obtained from KU-2-8/H and of a 0.025 M HCl solution was measured. The concentration of NIC in terms of functional groups $c_x = 0.038$ M was found by titration with an alkali solution. The substitution of the measured value $k = 0.35$ together with the equivalent electrical conductivities of the ions into Eq. (10) gave $\gamma = 0.28$. If the particles were spherical, then such a relative charge would correspond to $d = 22$ nm (the average distance of 1 nm between the nearest functional groups is substituted). The assumption of the shape of a particle as a tablet with a height h gave more realistic values: $h = 10$ and $d = 50$ nm.

Dynamics of exchange and retention of nano ion exchanger. For working with nano ion exchangers, it is convenient to use NIEX in the standard state—in the

form of water ions (NIC/H, NIA/OH) against the background of pure water: such a hydrosol can be easily quantitatively transferred to other forms, leaving pure water as a background using acid-base titration, e.g., if you want to get the sodium form of NIC, then an equivalent amount of NaOH solution is added to the NIC/H solution; if you want to get the chloride form of NIA, then an equivalent amount of HCl is added to the NIA/OH solution. In this regard, the crushed macro ion exchangers were previously converted into the form of corresponding water ions. Until the methods of restoring standard states are worked out, NIEX sols are irreversibly spent in working in ion-exchange processes. Below it is shown that standard states can be restored using reactions (3) and (4).

For the experimental implementation of the theoretical scheme corresponding to reaction (3), the breakthrough sorption curve of KU-2/H nanoparticles with the addition of an HCl electrolyte in a column with a AV-17/OH macro ion exchanger was recorded. The concentration of NIC in terms of functional groups $c_x = 0.038$ M, HCl concentration is 0.025 M; the volume of loading of the AV-17/OH macro anion exchanger in a column is 1 mL, column diameter is 4 mm, the free volume of the column is 1.71 mL; and the consumption of the mobile phase is 0.22 mL/min. As a result of the experiment, a modified bipolar layer with a capacity of 0.95 mEq/mL in anions and less than 0.1 mEq/mL in cations was obtained. The parameter p was less than 0.01.

Reaction (4) was carried out together with reaction (3) on a system of series-connected columns with AV-17/OH macro anion exchanger and KU-2/H macro cation exchanger (Fig. 6). The output sorption curves of NIC nanoparticles (KU-2) with a NaCl electrolyte were recorded. Electrical conductivity was measured (I) and the concentration of the chloride ion was measured by ion chromatography (2) (Tsvet-3006 chromatograph, DOKBA, Russia). The concentration of NIC in the volume range of the passed solution of 6–80 mL according to the results of titration with an alkali was 0.038 mEq/mL. As a result of the experiment, in the specified interval of the elution curve, a pure NIC/H form was obtained against the background of deionized water. Thus, the described process ensures the restoration of the standard state of the hydrosol.

To implement reaction (6), an elution curve of the NIA AV-17/OH hydrosol sorption was recorded on a column with a KU-2/H macro ion exchanger with a grain size of 0.45 mm. The absorbance of the solution was measured at the wavelength $\lambda = 315$ nm. As a result, the capacity of KU-2 was determined by NIA: 0.002 mEq/mL. This value corresponds to the RSC of the macrocation 0.07%.

Solid-phase ion exchange. The principal possibility of reaction (5) is shown in an experiment, in which a NIEX hydrosol containing no electrolyte was used to

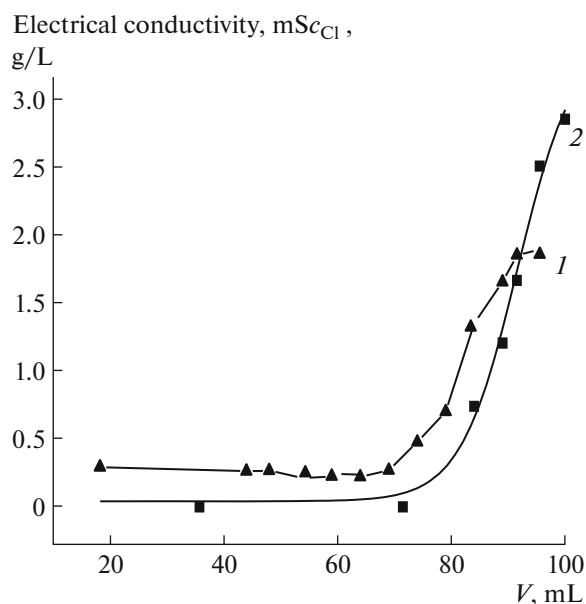


Fig. 6. Elution curve of the sorption of a hydrosol of KU-2 (NIC) nanoparticles contaminated with a NaCl electrolyte on a system of series-connected columns with an AV-17/OH macro anion exchanger and a KU-2/H macro cation exchanger. (1) Electrical conductivity and (2) the concentration of chloride ion were measured by ion chromatography.

transfer counter-ions from one column to another (Fig. 7).

The experimental installation contained two successively located identical columns with a strong base AV-17 \times 8 resin with a grain size of 0.3–0.5 mm in different ionic forms: the first in the chloride form and the second in the hydroxyl form. The volume of loading of columns with an internal diameter of 4 mm was 6 mL. Through this system of columns, an AV-17 NIA hydrosol purified from impurities of electrolytes, which had an OH-form at the entrance, was passed. The concentration of the hydrosol was 0.0025 mEq/mL. At the exit of the second column, the solution was collected and the fraction of the OH form of the released hydrosol, which was always defined as 100%, was determined by titration with acid. After passing 50 mL of a sol (flow rate of 0.7 mL/min), the process was stopped. By the regeneration of the second column with an alkali, the amount of the transferred chloride ion was determined. This amount (washed out by 0.130 ± 0.005 mEq of chloride ion) was strictly equivalent to the amount of the passed hydrosol (0.125 mEq, 2% of the capacity), which clearly proves reaction (5). Regeneration was performed with 0.1 M NaOH, 145 mL were passed, and the flow rate was 0.7 mL/min.

Use of nanosized ion exchangers in analytical chemistry. At present, ion chromatography and capillary

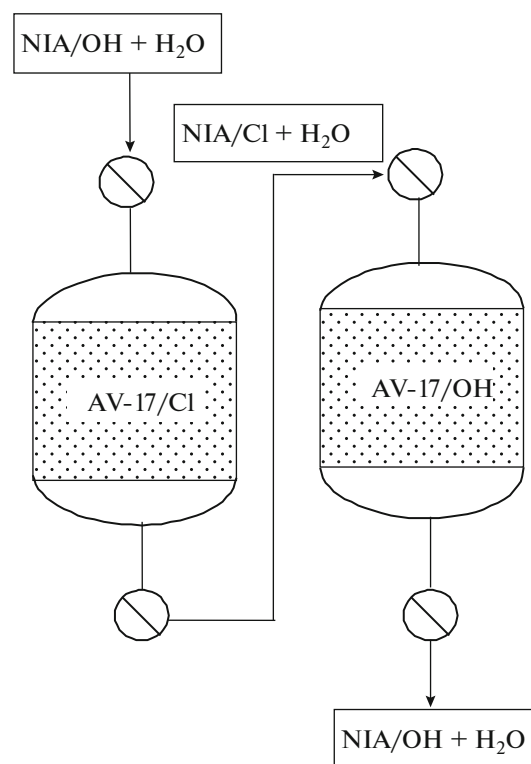


Fig. 7. Installation for the proof of reaction (5).

electrophoresis are well-developed methods, the problems with them are in expensive and insufficiently effective phases, insufficient selectivity, linearity and sensitivity, which results in the low productivity and high cost of ion analysis. The solution of such problems is possible, when NIEX phases, the distinctive feature of which are high equilibrium and kinetic properties, surface inactivity, are used as modifiers.

Unlike conventional ion exchangers, NIEX can pass through macroporous membranes and filter materials, and the presence of a large charge at a small mass makes it possible to control their movement and distribution at the phase boundaries.

Ion chromatography on a NACATEX cation-exchange column. The idea of modifying the surface of particles of micron-sized column loading with a suspension of submicroparticles by the electrostatic fixing of the latter on the surface has been known since the discovery of the method of ion chromatography and is constantly evolving [8–10]. When creating a cation-exchange NACATEX column, the formation of a structure of a sorption surface was achieved, the discriminant mark of which is the fixation of nanoparticles of the cationite-modifier in the pores of the anion exchanger-substrate [3, 11, 12]. The following basic principles have been implemented in our research [11, 12]:

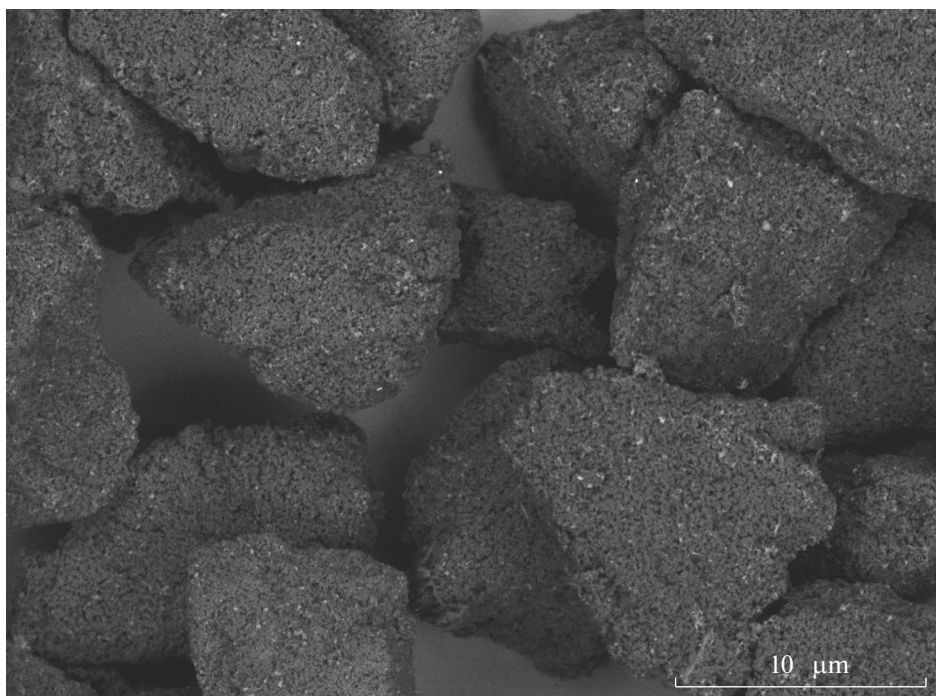


Fig. 8. Electron micrograph of grains of loading of NACATEX column (bright blotches correspond to particles of the modifier).

(1) a macroporous ion exchanger, the surface of which is composed of intrapore and outer surfaces, is chosen as the substrate;

(2) ion exchanger with the selectivity required for chromatography, the polarity of which is opposite to the polarity of the substrate, is selected as a modifier;

(3) the particle size of the modifier is chosen smaller than the pore size of the substrate to make it possible for particles to penetrate into the intrapore space;

(4) modification of the substrate is carried out in a dynamic mode, for which the nanosuspension of the modifier is passed through the chromatographic column filled with the substrate until its breakthrough into the filtrate;

(5) fixation of modifier particles on the surface of the substrate takes place by the mechanism of interaction of opposite electric charges;

(6) the ionic forms of the substrate and modifier provide the neutralization reaction in their interaction, which forms a sharp front of the dynamic process and a strong retention of nanoparticles in the pores of the substrate;

(7) the outer surface of the substrate is purified of the modifier by washing with water, ethanol, and concentrated solutions of acids and alkalis.

Figure 8 shows a micrograph of particles of the substrate, on which modifier blotches embedded in the macropores of the anion exchanger are visible. This type of surface structure is characterized by the stabil-

ity of its sorption properties and chemical stability, which is an advantage over the multifunctional silica gel-based sorbent described in [10].

In the test of the analytical properties of the chromatographic column on the ion chromatograph, the conditions for the separation and determination of alkali elements and the ammonium cation were cho-

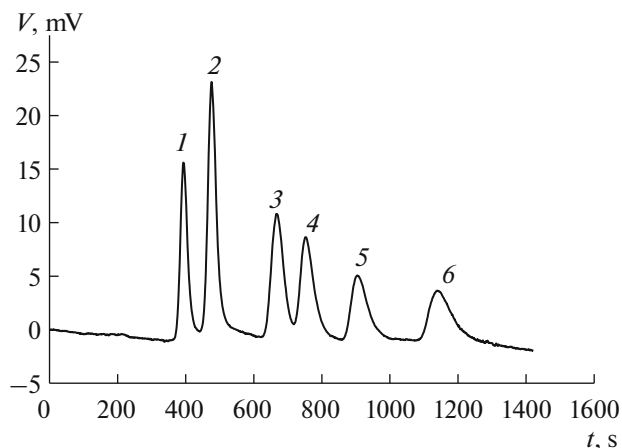


Fig. 9. Chromatogram of a model mixture of alkaline cations: (1) Li^+ (1 mg/L), (2) Na^+ (5 mg/L), (3) NH_4^+ (5 mg/L), (4) K^+ (5 mg/L), (5) Rb^+ (10 mg/L), and (6) Cs^+ (15 mg/L). Separation conditions: 150×4.6 mm NACATEX column, eluent: 2.5 mM HNO_3 , flow rate of 1.5 mL/min, conductometric detection with chemical suppression.

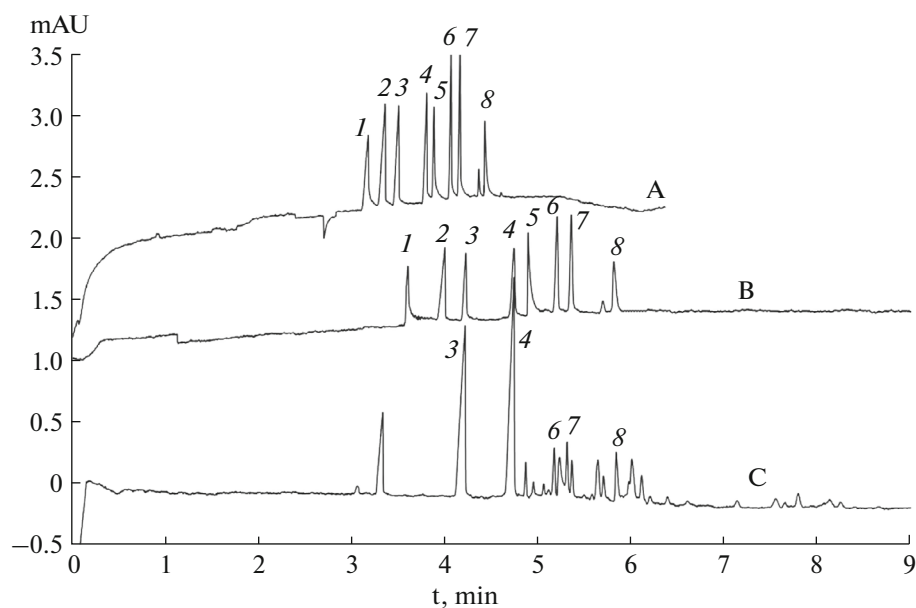


Fig. 10. Electrokinetic chromatogram of (A, B) a model mixture of anions of carboxylic acid and (C) wine sample diluted 200 times: (1) oxalate, (2) formate, (3) tartrate, (4) maleate, (5) citrate, (6) succinate, (7) lactate, and (8) acetate. Background electrolyte: 10 mM benzoic acid, 9 mM diethanolamine, 0.5 mM cetyltrimethylammonium bromide (CTAB). A—capillary was treated with CTAB; B, C—the capillary was treated with nano anion exchanger (NIA). Indirect UV detection, 254 nm.

sen. The limits of detection for analytes were tens of $\mu\text{g/L}$. Experimental parameters: separation column NACATEX 150×4.6 mm, suppressive column with AV-17 $\times 8$ anion exchanger in OH form, eluent 2.5 mM HNO_3 ; flow rate 1.5 mL/min. The chromatogram is shown in Fig. 9.

Capillary electrophoresis. In the works by Kartsova et al. [13, 14], the NIA sample prepared by us was used as a modifier of the background electrolyte in capillary electrophoresis and capillary walls in electrokinetic chromatography to separate mixtures of inorganic and organic anions. The effect of nano ion exchanger con-

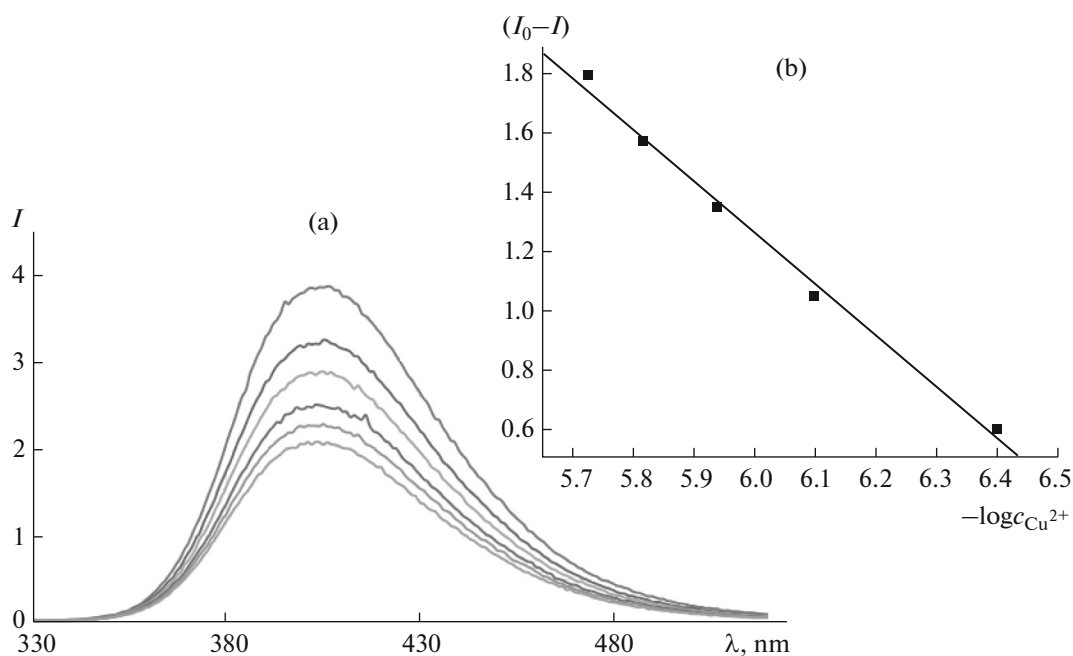


Fig. 11. (a) Luminescence spectra of NIA in the form of sulfosalicylate with additions of copper ions and (b) calibration curve.

centration in the composition of the background electrolyte on the magnitude and sign of the electroosmotic flow, as well as the efficiency and resolution factors in the electrophoretic separation of inorganic anions, were revealed. It was found for the first time that the addition of a strong base nano anion exchanger to the background electrolyte in a concentration exceeding 0.01 mM in functional groups results in the inversion of the electroosmotic flow. This indicates a dynamic modification of the walls of the quartz capillary and results in an increase in the efficiency and selectivity of the separation of inorganic anions as compared with the results obtained with the traditional cationic detergent cetyltrimethylammonium bromide. The selective and highly efficient separation of mixtures of inorganic and organic anions using NIA was demonstrated. The procedure was used to determine organic acids in wine (Fig. 10).

Photoluminescence of nano ion exchanger. Heavily diluted NIEX solutions on a polystyrene substrate are luminophores. The strongest signal corresponds to the NIEX in the standard state. Some ionic forms that are widespread in nature do not affect this signal, but the forms containing transition metal atoms quench it [15]. Particles of NIEX repeatedly concentrate such ions; therefore, the samples into which the NIEX is dosed can be analyzed by the luminescence method with high sensitivity [16]. A new method for determining heavy metals in waters is based on the principle of luminescence quenching and is indirect with a limited dynamic range (1–2 orders of magnitude in analyte concentration), which can be attributed to its shortcomings. Its advantages lie in the ability to move the dynamic range by choosing a metered amount of NIEX and in versatility with respect to various heavy metals.

A possibility of determining copper (II) was studied. For this purpose, NIA was previously converted into sulfosalicylic acid anions (SSA). Model solutions contained 26 μM NIA/SSA, in which Cu^{2+} ions with concentrations of 0.4–2 μM were dosed. The luminescence spectrum had a maximum at 405 nm (Fig. 11a). The analytical signal of copper ions was the difference between the pure water signal (I_0) and the sample. The calibration curve (Fig. 11b) was approximated by the equation $I_0 - I = 11.71 + \log c_{\text{Cu}^{2+}}$, where $c_{\text{Cu}^{2+}}$ was the concentration of copper ions, M.

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