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Organic Ion Exchangers. Synthesis and Their Behaviour in the Retention of Some Metal Ions

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Summary: Three pyridine strong base anion exchangers as beads were obtained by quaternization reactions of a 4-vinylpyridine : 8% divinylbenzene copolymer of gel type. These resins possess methyl / ethyl / butyl radicals as substituents on N^+ atoms and have exchange capacities of 4.80 mEq/g and 2.10 mEq/mL. For pyridine strong base anion exchangers, the behaviours in the retention processes of Cr(VI) as oxyanions and Ga(III) as $[GaCl_4]^-$ complex anion were evaluated with the bath method. All the resins exhibited retention properties, but the retained amounts of the metal cations are different as a function of the alkyl length as substituent on N^+ atoms and the complex anion nature. Thus, Cr(VI) oxyanions are best retained by the resin with $-CH_3$ as substituent on N^+ atoms while $[GaCl_4]^-$ complex anion by the resin with $-C_4H_9$ as substituent on N^+ atoms. By aminolysis reaction of an ethylacrylate : acrylonitrile : divinylbenzene copolymer as beads of macroporous type with $NH_2OH \cdot HCl$ in the presence of C_2H_5OH a new chelating ion exchanger was performed which contains both amidoxime and hydroxamic acid functional groups. This ion exchanger has the retention property for different metal cations but its retention capacities values are strongly dependent of the nature of metal cation and the counterion as well as pH of the solution. Thus, in the static conditions Zn(II) cation with NO_3^- anion as counterion is retained with the best result at $pH = 5$. As an example, for the aqueous metal cation solution of 10^{-2} M concentration for $Zn(NO_3)_2$ the resin possess at equilibrium a retention capacity of 6.70 mmol Zn/g dry resin and for Cu(II) from $Cu(NO_3)_2$ solution of same concentration, the retention capacity is 0.22 mmol Cu/g dry resin and Fe(III) from $Fe(NO_3)_3$ solution is not retained.

Keywords: adsorption; functionalization of polymers; ion exchangers; metal-polymer complex; resin

Introduction

Organic ion exchangers, as known, are three-dimensional covalent networks, so-called matrices, that contain exchangeable ions associated with fixed acid or basic groups. These ion exchangers can be chemically modified natural or synthetic products.

Synthetic organic ion exchangers are the most suitable ion exchange materials because of their well defined physical forms (granules, beads and fibres) and their very various chemical and morphological structures[1].

Until 1950, the four principal types of ion exchangers were more commercially available following: acid, strong – base, weak – base resins based on styrene : divinylbenzene copolymers that possess sulfonic acid groups, benzyltrimethylammonium chloride / benzyldimethyl-2-hydroxyethylammonium chloride groups, primary / secondary / tertiary amines groups, respectively, as well as weak – acid resins which contain carboxylic groups that they proceed from acrylic / methacrylic acid : divinylbenzene copolymers[2].

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In the meantime a lot of ion exchange resins were performed.

A careful analysis of the literature data shows that the studies on organic ion exchangers (resins) are focused to (i) the synthesis of matrices with new chemical structures and different morphologies; (ii) the achievement of new functional groups attached to known matrices; (iii) the establishment of some relationships between the chemical and morphological structures of the resins, their retention properties of different ionic species and the retention experimental conditions, especially the required pH for the aqueous medium to have the best retention capacities; (iiii) the study of the different polymerization techniques for the achievement of monodisperse spherical particles, in the case of the resins as beads.

One among the applications of the ion exchangers is the retention of metal cations which occurs in the deionization process of surface water, the removal of cations of toxic metals from industrial effluents, the recovery of interesting metals from rinse waters from some industries such as galvanic and electronic industries, the separation of precious metals as well as recovery and purification of radioactive ions from acid aqueous solutions, etc. The retention of metal cations occurs both by ion exchange and chelating processes.

The first process is involved in the case of the cation exchangers as well as in the case of strong base anion exchangers, if the metal cations are as complex anions or there are conditions to form these anions.

The chelating processes can appear when ion exchangers contain into their functional groups one or more electron-donor elements, i.e., N, S, O and P, such as amine, thiol, thiouronium, iminodiacetate, aminophosphonate, amidoxime groups, etc.

The present paper shows on the syntheses of new strong base pyridine anion exchangers and acrylic mixed ion exchanger. The last product contain together both base character groups by amidoxime ones and acid character groups due to hydroxamic acid groups.

For all the performed ion exchangers their behaviours in the retention processes of different metal cations by bath method were determined.

Morphology

Pyridine Strong Base Anion Exchangers

It is known the achievement of a material in the bead form with ion exchange properties having 4-vinyl-1-methylpyridinium chloride structural units.

Generally, these exchangers are performed by the quaternization with reactive alkylation reagents of 4-vinylpyridine – divinylbenzene (4-VP – DVB) copolymers.

The manufacturer's data suggest a better stability to chemicals, radiation and temperature for pyridine strong base anion exchangers by comparison to common those based on styrene - divinylbenzene copolymers.

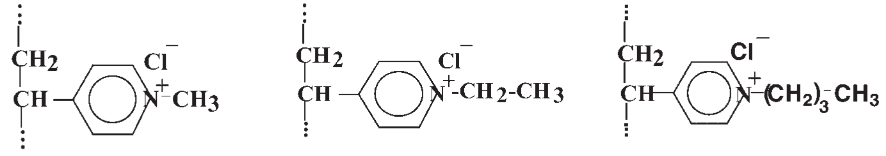
For this reason, probably, the pyridine strong base exchangers are used to recovery and purification of uranium and plutonium [3–7], sugar purification operations[8] and they also could be potential ion exchange materials for the water purification[9].

In the present study pyridine strong base exchangers with different alkyl substituents on N^+ atoms were synthesized because it is known that styrene strong base anion exchangers have their affinity towards different anions as a function of the chemical nature of the substituents on N^+ atoms[10,11].

The synthesized pyridine exchangers and their weight and volume ion exchange capacities are shown in Scheme 1.

All the three pyridine anion exchangers were performed based on a 4-VP : 8% DVB gel type copolymer.

Subsequently, the behaviours of PSBA-1, PSBA-2 and PSBA-3 in the retention process of Cr(VI) as CrO_4^{2-} oxyanions [12,13] as well as Ga(III) [14,15], Hg(II), Pb(II), Zn(II), Cu(II), Mn(II) and Ni(II) [16] as respective chlorocomplexes were analyzed. Ion exchange samples were sieved at a particle size of



PSBA-1 ($C_W = 4.30$ meq/g; $C_V = 1.75$ meq/mL)

PSBA-2 ($C_W = 4.80$ meq/g; $C_V = 2.10$ meq/mL)

PSBA-3 ($C_W = 4.50$ meq/g; $C_V = 2.05$ meq/mL)

Scheme 1.
Synthesized pyridine strong base anion exchangers

0.4–0.8 mm. The CrO_4^{2-} oxyanions was retained from K_2CrO_4 aqueous solutions and the other cations from their chlorides in 6 M HCl, where respective chlorocomplexes exist. All retention experiments were performed under static conditions at room temperature (25 °C ± 2 °C).

For the retention study of CrO_4^{2-} the ion exchange samples were used both in Cl^- and SO_4^{2-} forms. From Figure 1–3 can be seen the following aspects:

(1) the resins in the Cl^- form show a maximum retention between 200–400 mg Cr/L aqueous phase, then a continuous decrease of the retention capacities with the increasing of Cr(VI) amount is observed, whereas the resins in SO_4^{2-} form exhibit a continuous increase of retention over the whole Cr(VI) concentration domain;
(2) the resins in Cl^- form exhibit considerable differences of their retention capacities while the resins in SO_4^{2-} form have close values for the retention capacities;
(3) indifferently of its ionic form, the PSBA-1 resin, namely the resin which posses $-CH_3$ as substituent on N^+ atoms, therefore the resin with the highest hydrophilic structure, exhibits the greatest preference for Cr(VI) oxyanion species. As recommendation for the retention process of Cr(VI) as oxyanions if the Cr(VI) amount in the aqueous phase is below 400 mg Cr(VI)/L is indicated the using PSBA-1 resin in Cl^- form and after this Cr(VI) amount the SO_4^{2-} form of this resin is required.

The following studies show that the three pyridine strong base anion exchangers have different behaviours in the Ga(III) retention than those in the Cr(VI) retention. In these experiments both pyr-

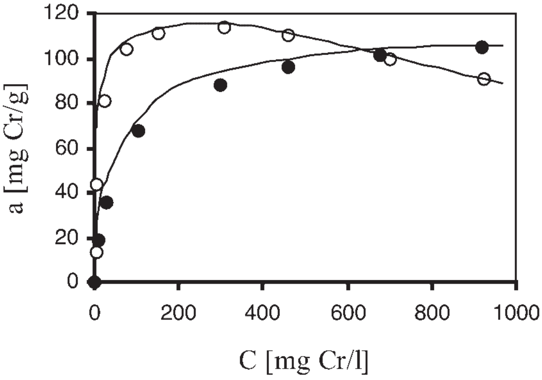


Figure 1.
Uptake of Cr(VI) on the pyridine resin with methyl substituent at N^+ in the Cl^- form (○) and SO_4^{2-} (●) as a function of Cr(VI) concentration solution at equilibrium

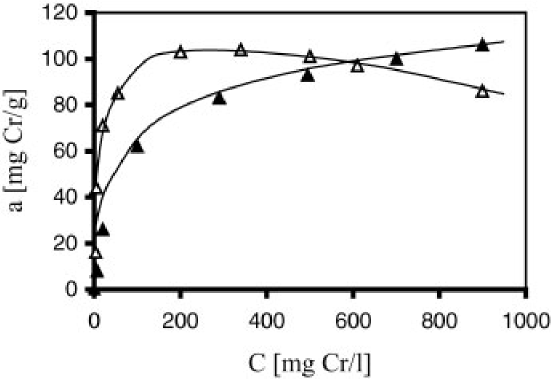


Figure 2.
Uptake of Cr(VI) on the pyridine resin with ethyl substituent at N^+ in the Cl^- form (△) and SO_4^{2-} (▲) as a function of Cr(VI) concentration solution at equilibrium

idine and styrene (Amberlite IRA 400) resins were used in the Cl^- form. Thus, in the Ga(III) retention, the PSBA-3 resin, i.e., the resin the resin with $-C_4H_9$ substituent on N^+ atom that means the resin with the highest hydrophobic character, exhibits greater retention (Table 1).

In contrast to retention studies of Cr(VI) oxyanions when the highest retention capacity was attained by the pyridine strong base anion exchanger with highest hydrophilicity (PSBA-1), those for $[GaCl_4]^-$ ions show the preference of PSBA-3, the resin with highest hydrophobic structure, for these anions.

The data listed in Table 1 also show that the 6 M HCl solution is more suitable than the water for the retention of Ga(III). This is a normal situation because Ga(III) in 6 M HCl exists as $[GaCl_4]^-$ complex anions and the retention mechanism by a strong base anion exchanger can occur especially by an ion exchange process.

The superiority of the PSBA-3 is also observed from maximum retention capacities determined by Langmuir isotherms of the three pyridine resins. These capacities are 44.44, 38.00 and 60 mg Ga(III)/g dry resin for PSBA-1, PSBA-2 and PSBA-3, respectively.

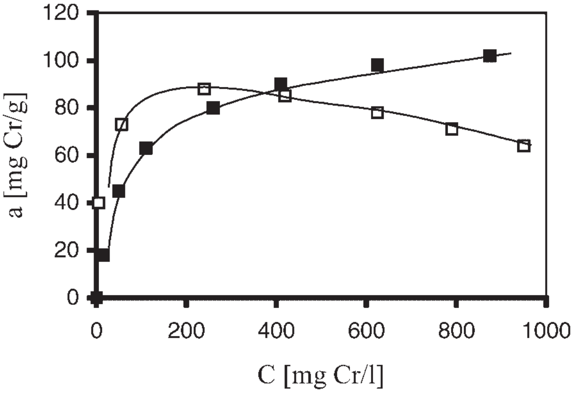


Figure 3.
Uptake of Cr(VI) on the pyridine resin with butyl substituent at N^+ in the Cl^- form (□) and SO_4^{2-} (■) as a function of Cr(VI) concentration solution at equilibrium

Table 1.
Values for the distribution coefficients (K_d) for the three pyridine resins in comparison to a styrene commercially available strong base anion exchanger

Resin	Liquid phase	K_d (g · mL)
PSBA-1	6 M HCl	669.35
	Water	147.68
PSBA-2	6 M HCl	959.10
	Water	138.26
PSBA-3	6 M HCl	7339.14
	Water	160.90
Amberlite IRA 400	6 M HCl	3634.03
	Water	150.26

Acrylic Ion Exchangers

Most commercially available acrylic ion exchangers are the weak acid exchangers which possess –COOH groups that proceed from acrylic acid / methacrylic acid : divinylbenzene copolymers and weak base exchangers having amine groups.

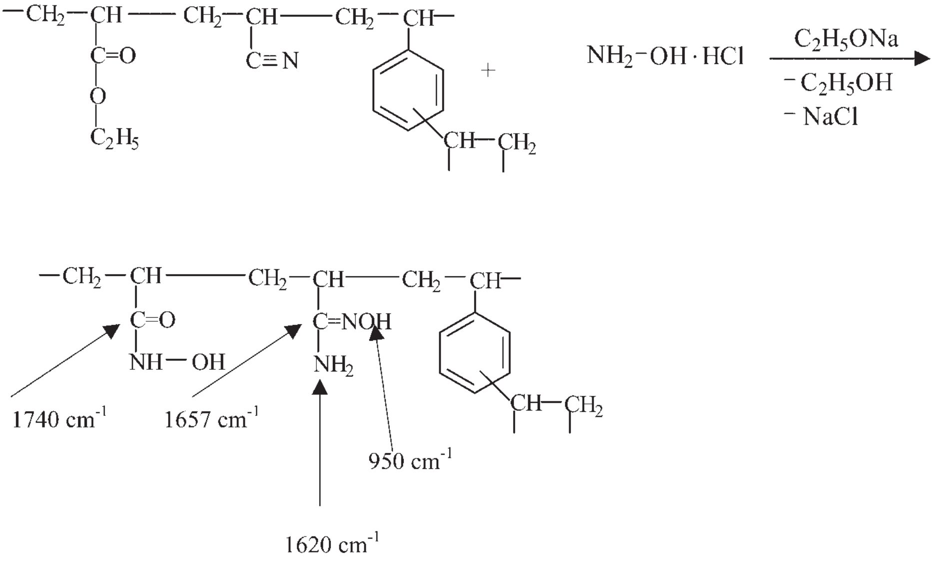
Different studies show the achievement of the acrylic weak base exchangers only with amidoxime groups. One among these is that performed by the reaction with NH_2OH of different acrylonitrile : divinylbenzene copolymers[17].

Other studies show on the achievement of resins with hydroxamic acid groups performed by the reaction with NH_2OH of alkyl acrylate groups from different precursors[18].

In the present study a resin which possess both amidoxime and hydroxamic acid was performed by the reaction with $NH_2OH \cdot HCl$ of a copolymer 20% acrylonitrile : 70% ethylacrylate : 10% divinylbenzene[19].

The resulting resins was characterized by IR spectra and total (weak base and weak acid) exchange capacities. Because of different amounts of monomers in the A/B/C terpolymer, the major part of total exchange capacity represents the weak acid exchange one.

Scheme 2 shows the structure of the resin, the assignment of the main characteristics absorption bands of the functional



$C_W = 3.89$ mEq/g

$C_V = 1.20$ mEq/mL

Scheme 2.
Synthesis of the resin with amidoxime and hydroxamic acid groups

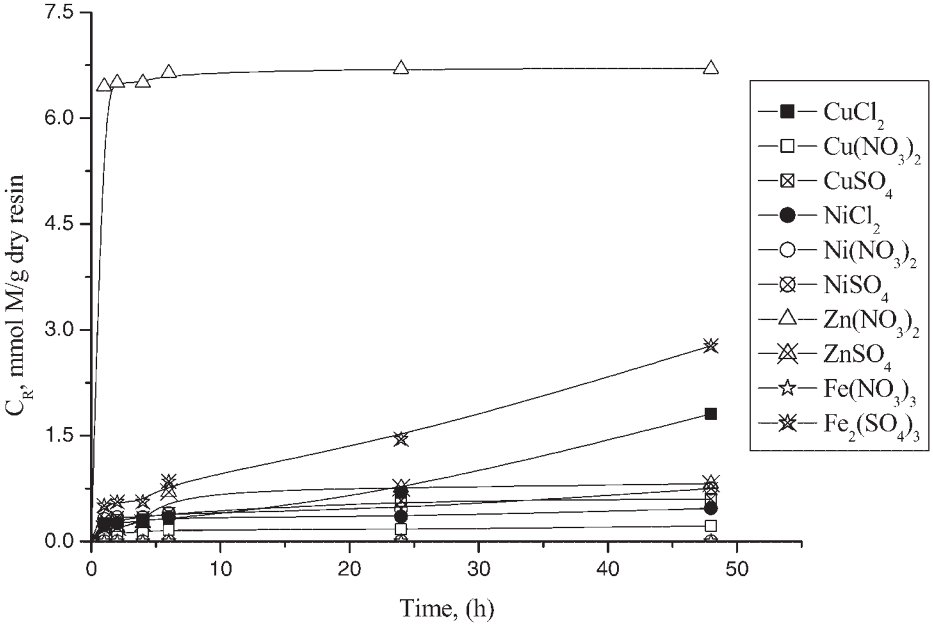


Figure 4.
Retention of some metal cations on the resin with amidoxime and hydroxamic acid groups

groups from IR spectrum and the values of the exchange capacities.

The performed copolymer beads contain only A/B/C terpolymer, the unreacted ethylacrylate and acrylonitrile are not present in the reaction product.

The data from Scheme 2 permitted us to affirm that the aminolysis reaction of ethylacrylate : acrylonitrile : divinylbenzene terpolymer with hydroxylamine in the presence of sodium ethoxylate led to an ion exchanger which possess amidoxime and hydroxamic acid groups.

For this resin was analyzed its behaviour in the retention of some metal cations, such as Cu(II), Ni(II), Zn(II), Fe(III), Pb(II), Mn(II) and Cd(II) both at $pH = 2$ and $pH = 5$. All the experiments were performed in the static conditions at room temperature.

From this analysis the following aspects are observed:

- the retentions at $pH = 2$ are lower than those at $pH = 5$;
- Cd(II) is not retained both $pH = 2$ and $pH = 5$;
- the counterion of metal cations have a major role in the retention process.

Figure 4 shows the data from the retentions of Cu(II), Ni(II), Zn(II) and Fe(III) from their different salts at $pH = 5$.

From Figure 4 can be observed that the highest retention is performed in the case of Zn(II) cation when it has as counterion NO_3^-. It should be note that the retention equilibrium in this case is reached at 60 min, this aspect means a fast retention process.

Conclusion

By quaternization reactions of a 4-vinylpyridine : 8% divinylbenzene copolymer of gel type pyridine strong base anion exchangers which possess methyl / ethyl / butyl substituent on N^+ atoms were performed. These anion exchangers have higher or equal exchange capacities towards those of commercially available styrene strong base anion exchangers. As expected, pyridine strong base anion exchangers synthesized in this study have retention properties of different metal cations when they exist as complex anions such as Cr(VI) oxyanions and $[GaCl_4]^-$. The values of the retention capacities are strongly dependent of N^+ substituent length : complex anion nature relationship. Thus, for the retention of Cr(VI) oxyanions it is suitable the using of the pyridine strong base anion exchanger which possess $–CH_3$ as substituent on N^+ while the $[GaCl_4]^-$ retention with the highest value occurs using the pyridine strong base anion exchanger having $–C_4H_9$ substituent on N^+ atoms.

By aminolysis reaction of a ethylacrylate : acrylonitrile : divinylbenzene terpolymer with $NH_2OH \cdot HCl$ a new chelating ion exchanger which possess both amidoxime and hydroxamic acid functional groups was performed.

The behaviour of this resin in the retention process of some metal cations varies as a function of solution pH and the counterion nature of the respective cations. Thus, in the static conditions Zn(II) cation with NO_3^- anion as counterion is retained with the best result at $pH = 5$. As an example, for the aqueous metal cations solution of 10^{-2} M concentration for $Zn(NO_3)_2$ the resin possess at equilibrium a retention capacity of 6.70 mmol Zn/g dry resin, for Cu(II) from $Cu(NO_3)_2$ solution, the retention capacity is 0.22 mmol Cu/g dry resin and Fe(III), from $Fe(NO_3)_3$ solution, is not retained.

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