

TRENDS IN WEAK BASE ANION EXCHANGERS RESINS

Cornelia LUCA, Cristina Doina VLAD* and Ion BUNIA

“Petru Poni” Institute of Macromolecular Chemistry, Aleea Grigore Ghica Voda, 41A, Iași - 700487, Roumania

Received February 5, 2008

The definition and some characteristic concepts regarding ion exchangers are pointed out. A classification of organic ion exchangers, according to several criteria, with location of the weak base anion exchangers in this classification is proposed. Beginning with characteristic reactions, some peculiarities of weak base anion exchangers and continuing with classical methods of achievement of these ion exchangers is further presented. Finally, trends in the field of organic weak base anion exchangers are shown. They are with regard to various morphologies and different shapes of the matrix as well as special structures of the amine moieties. The applications for each class of weak base exchangers are briefly discussed.

GENERAL CONSIDERATIONS. DEFINITION AND BACKGROUND

Ion exchangers, in general, are insoluble solid materials which carry exchangeable cations or anions. Therefore, an ion exchanger may be regarded as a crosslinked/three dimensional network called matrix/framework with fixed charges, electroneutrality is due to equal number of low ions of opposite sign called counter-ions. They are free to move within the matrix and can be replaced by other ions of the same sign when the ion exchanger is in contact with an electrolyte solution. The ion exchange, which is characteristic property of an ion exchanger, is due to counter-ions. Inorganic and organic ion exchangers are known but this paper will show only on organic ion exchangers.¹⁻⁶

Organic ion exchangers are crosslinked covalent networks, so-called matrix, that contain acid or base functional groups. Synthetic organic ion exchangers are obtained by the two principal reactions used to produce polymeric material, namely polycondensation and addition polymerization of some comonomers. The incorporation of a trifunctional comonomer in polycondensation reactions is required while in polymerization, the presence of a bifunctional comonomer is sufficient.

Generally, the polymerization structures are made by two ways: (i) the polymerization of a monovinyllic monomer which contains a basic or

acidic group with a divinyllic monomer; (ii) the achievement of a neutral network, called the precursor or starting material, followed by the introduction of basic or acidic groups by suitable polymer analogous reactions.

The polymerization only of the two monomers leads to the ion exchangers so-called of gel type while the addition of an appropriate inert compound in the mixture of comonomers leads to the ion exchangers of porous type.

The ion exchangers which contain cations or anions as counter-ions are called cation exchangers or anion exchangers, respectively. They can be weak and strong cation exchangers as well as weak and strong anion exchangers. The matrix of a cation exchanger may be regarded as a macromolecular polyanion whereas that of an anion exchanger as a polycation.

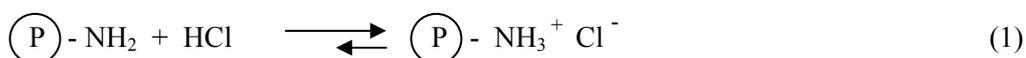
The exchange capacity, is the most important property in the understanding the work with the ion exchangers.

The total capacity indicates the number of fixed charges per specified amount of ion exchanger. It can be described as both weight capacity and volume capacity, having as units milliequivalents per grame of dry ion exchanger ($\text{meq}\cdot\text{g}^{-1}$), and milliequivalents per cubic centimeter of fully swollen exchanger ($\text{meq}\cdot\text{cm}^{-3}$), respectively. This capacity is a constant for the material and does not depend on the experimental conditions.

* Corresponding author: cdvlad@icmpp.ro

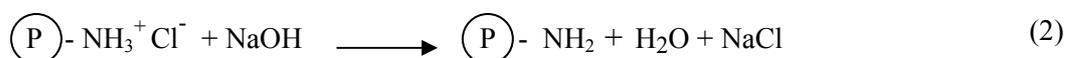
The effective capacity is the number of exchangeable counter-ions per specified amount of exchanger. For this capacity the same units are used as those above mentioned and it depends on the experimental conditions being, generally, lower than total capacity.

It should be mentioned that the ion exchangers which contain fixed positive charges, therefore, negative counter-ions are called anion exchangers whereas those which contain fixed negative charges are cation exchangers. Materials with both positive and negative fixed charges are also known, they being called amphoteric ion exchangers. More recently these ion exchangers are called bipolar electrolyte-exchange resins (BEE) or zwitterionic ion-exchangers.^{7,8}



The reaction to left is, in fact, the hydrolysis of the hydrochlorides of the amines in the aqueous media. This hydrolysis occurs in a higher or lower degree as a function of the amine basicity.

Weak base anion exchangers do not split neutral salts like NaCl or Na₂SO₄.



Because of the weak basicity, these anionic exchangers are easily to regenerate. For the regeneration is need of only a slightly higher level than the theoretical exchange capacity. In despite of their ease of regeneration, they suffer of the drawback that the captured acids can be easily eluted. (The reaction from the right to left according to equation (1)).



Corresponding to the coordination properties both of the resin and the metal, one ion can be linked to one, two or even more nitrogen atoms⁹. Alkaline earth ions do not have comparable Lewis acid properties. As a consequence, they are excluded from the adsorption and an extreme selectivity for heavy metals is observed. Among different heavy metals there is a series of selectivity.^{10,11}

The present paper will deal on weak base anion exchangers.

REACTIONS OF THE WEAK BASE ANION EXCHANGERS

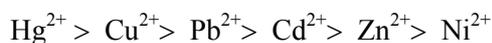
Weak base anion exchangers possess primary, secondary and/or tertiary amine groups as functional groups attached to matrix. At neutral pH the nitrogen atoms of these groups are non protonated. Therefore, they have a free electron pair and can act as Lewis bases.

In fact, a weak base anion exchanger is an adsorbent for strong acid, it takes up acids without exchanging ions according to equation (1).

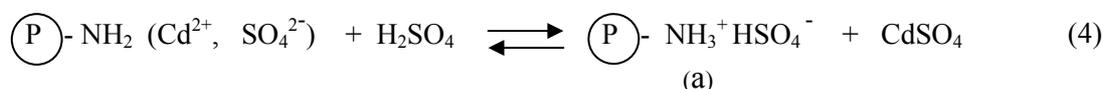
An important property of the ion exchangers is their participation to many use → regeneration sequences.

The equation (1) shows an use process of the weak base anion exchangers while the regeneration occurs according to equation (2).

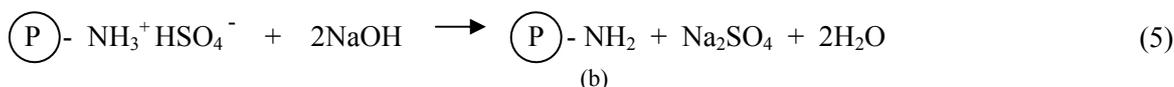
Another reaction of these anion exchangers is the retention by coordination bonds of Lewis acids like heavy metal cations. As an exemple, the retention of cadmium sulfate can be written as equation (3).



However, the nitrogen atoms of the amine groups strongly prefer the retention of strong acids over that of heavy metal cations. Consequently, the regeneration of the exchanger can be achieved by means of a strong acid (equation 4).



In the acidic form, i.e., (a) form, the exchanger can not be reuse for the retention of heavy metal cations by coordination process. For this the ion

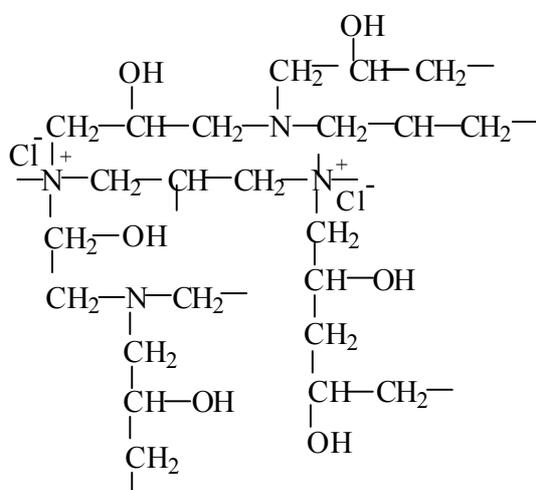


CLASSICAL REACTIONS FOR THE ACHIEVEMENT OF WEAK BASE ANION EXCHANGERS

The first commercial anion exchanger was of weak base type called Wolfatit M obtained by the polycondensation of m-phenylenediamine and polyethyleneimine with formaldehyde. Similar

exchanger must reconverted to the free base form (form (b) from equation 5), e.g. by means of NaOH.

polycondensation products were later manufactured in different countries and such products are still produced commercially. As an example are those obtained from the polycondensation of the epichlorhydrine with polyamines as: ethylenediamine, diethylenetriamine, triethylenetetramine, etc, with a chemical structure shown in Scheme 1.¹²



Scheme 1. Chemical structure of an epoxy-type base anion exchanger.

The most readily available commercial weak base exchangers are the polymerization structures based on polystyrene or acrylic matrices containing primary, secondary or tertiary amine groups, or all these groups together. These structures are depicted in Scheme 2.

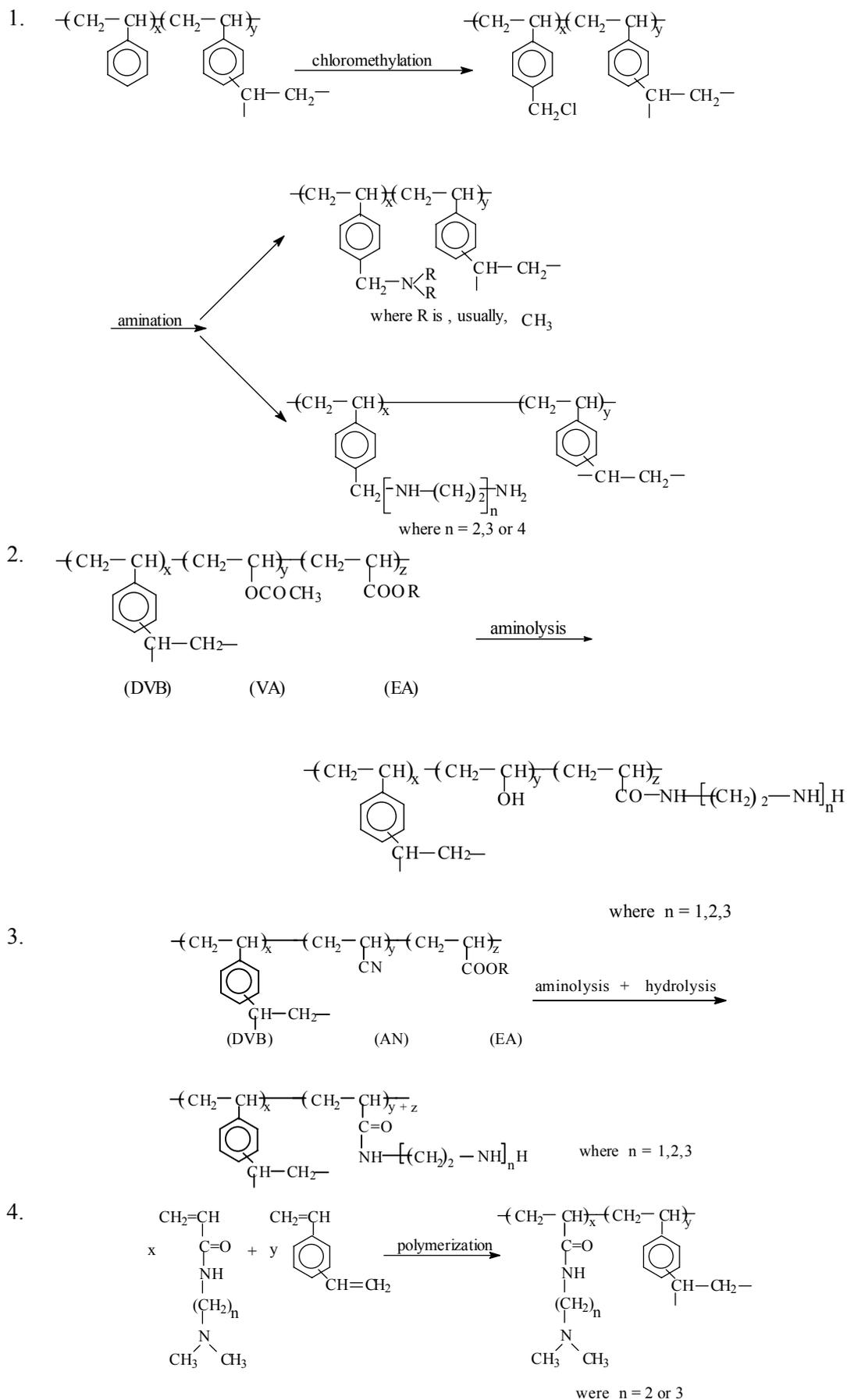
The styrene based weak base exchangers are obtained by the chloromethylation reaction followed by the amination with dimethylamine or polyamine (reaction 1, Scheme 2).

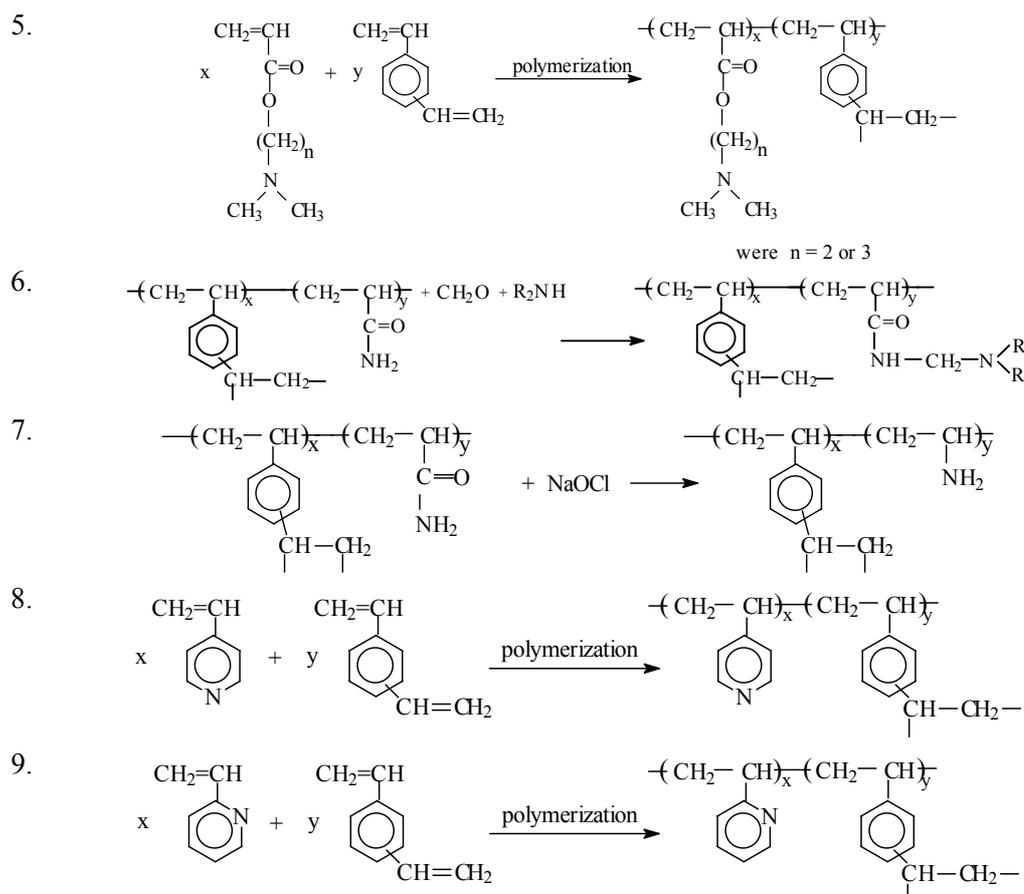
An undesirable side reaction can also take place. This is the reaction between the pre-attached amine groups with $-\text{CH}_2\text{Cl}$ groups. It can take place intra- or inter- chain, but both situations can occur. Both side reactions lead to the decrease of ion exchange capacity of the performed ion exchangers while the inter-chain side reaction, in addition, leads to the increase of the crosslinking degree of the matrix of the respective ion exchanger. By using a large excess of amine, the side reaction is greatly reduced.

Generally, the styrene based weak base exchangers possess large exchange capacities, have high regeneration efficiency and high chemical stability.

More generally, they are used to produce water with quality required by any industrial process starting from polluted influent water whose characteristics are not appropriate to a specific application. Thus, these anion exchangers remove heavy metal cations from wastewaters, organic pollutants with acidic character (free acids, some phenols), catalyses, etc.^{13,14}

The reactions (2) and (3) are the most common preparation methods of acrylic weak base anion exchangers. Generally, the aminolysis yield values of the DVB-VA-EA copolymers, are higher than ones obtained for the DVB - AN - EA copolymers, possibly due to the autocatalytic effect of the hydroxyl functional groups formed by the chemical modification of the acetate functional groups.¹⁵





Scheme 2. Some reactions for the preparation of weak base anion exchangers.

The acrylic weak base anion exchangers exhibit a higher hydrophilic character than those based on styrene: DVB copolymers. Thermal and chemical stabilities of these exchangers were analyzed.^{16, 17}

Thermal stability depends on the nature of both the copolymer and the amine used in the aminolysis reaction. The weak base exchangers are with lower thermal stability than their precursor copolymers.

Chemical stability in aggressive media was determined in: HCl, NaOH, H₂O₂, NaOCl+NaOH and NaOCl +FeSO₄ aqueous solutions. This study shows that the acrylic anion exchangers with a lower hydrophilicity have a higher chemical stability, therefore the acrylic weak base anion exchanger yielded from aminolysis reaction with ethylenediamine exhibits the highest chemical resistance in the aggressive media studied. An important parameter in the chemical stability of an anion exchanger is also morphological structure of its matrix. Thus, the acrylic anion exchangers with permanent porosity have a higher resistance than those with the porosity in the swollen state.

For acrylic weak base anion exchangers, their behaviors in the retention of some metal cations

such as: Cu(II), Ni(II), Cd(II), Pb(II), Zn(II), Co(II) were analyzed.¹⁸⁻²³

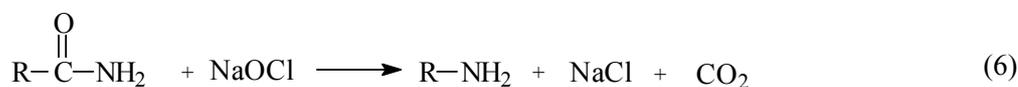
The aminolysis reaction was also used for the preparation of fibrous weak base anion exchangers being applied on polyacrylonitrile fibres.²⁴ Similar to the other fibrous ion exchangers, their main advantage compared to the granulation exchangers is a unique combination of extremely fast rate of sorption and easy permeability of their filtering layers for liquids.

The reactions (4) and (5) show also the methods of the preparation of acrylic weak base anion exchangers. In contrast to the reaction (2) and (3) which use suitable polymer-analogous reactions on acrylic copolymers, the reactions (4) and (5) use the polymerization between an acrylic monomer which contains an amine group and divinylbenzene. With reference to the chemical stability of the acrylic anion exchangers, those which contain amide groups possess a higher stability than that with ester group.

The reaction 6 (Scheme 4) depicts the preparation of some acrylic weak base anion exchangers by the Mannich reaction. These ion exchangers exhibit a very low chemical stability in

acidic and alkaline media because of the spacer of only one methylene group between amide and amine moieties.²⁵

It is well-known that NaOCl or NaOBr in alkaline aqueous solutions determines the trans-



This method is also used for the preparation of weak base anion exchangers^{26, 27} shown in Scheme 2 by the reaction 7.

The anion exchangers based on 4-vinylpyridine – divinylbenzene copolymers show better stability to radiation compared to conventional anion exchangers based on styrene-divinylbenzene copolymers. That is probably why pyridine anion exchangers are used in uranium and plutonium recovery as well as their purification²⁸⁻³². Generally, they are obtained as beads from the suspension polymerization technique and the porosity in the matrix is introduced by some inert organic liquids with comonomers at the time of polymerization.³³

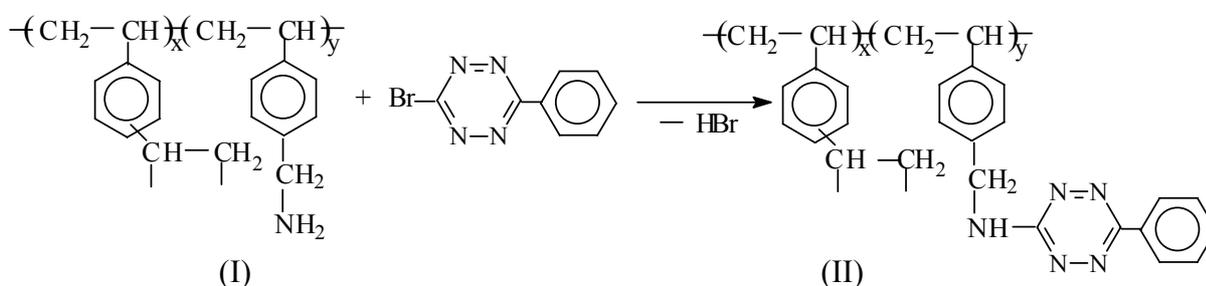
4-Vinylpyridine: divinylbenzene copolymers were used as sorbents for extraction of polar organic pollutants due to the polarity of these

formation of the amides to primary amines with the loss of one carbon atom. This reaction is called Hofmann degradation of the amides, according to equation (6).

sorbents because of the polarity of the comonomer 4-vinylpyridine. For good results in the extraction process a compromise is required between the percentage of 4-vinylpyridine, which increases the polarity of the sorbent, and the percentage of divinylbenzene, which increases the surface area.³⁴

SOME SPECIAL STRUCTURES OF WEAK BASE ANION EXCHANGERS AND THEIR APPLICATIONS

By reaction of an aminomethylated macroporous styrene-divinylbenzene copolymer with 3-bromo-6-phenyl-1,2,4,5-tetrazine was performed a 1,2,4,5-tetrazine modified weak base anion exchanger.³⁵



Scheme 3. Chemical structure of a styrene tetrazine-modified weak base anion exchanger.

The ion exchanger (II) behaves as a weak base anion exchanger due to protonation of the secondary amine spacer in an acidic aqueous solution.

For weak base exchangers I and II the sorption properties of the anionic metal chlorocomplexes of some precious metals as Ir(IV), Au(III), Pt(IV), Os(IV), Ru(III), Pd(II), Rh(III) and some base metals Zn(II), Cd(II), Fe(III), Co(II), Ni(II), Cu(II) in dilute hydrochloric acid media were determined.

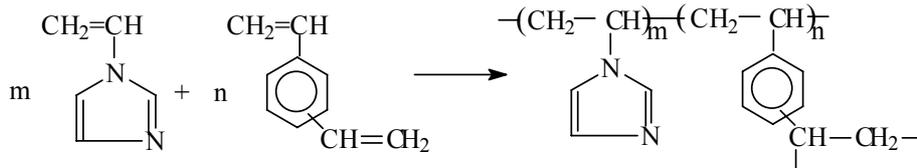
In 1M HCl medium the following affinity order was observed:

weak base anion exchanger I : Au(III)~Ir(IV)> Os(IV)>Pt(IV)>Pd(II)>Ru(III)>Rh(III)

weak base anion exchanger II : Au(III)~Ir(IV)> Os(IV)>Pt(IV)>Pd(II)>Ru(III)>Rh(III)

The increased retention of $[\text{PdCl}_4]^{-2}$ anion by the tetrazine weak base ion exchanger II could not be explained by a simple ion – exchange process. In this case an undoubted coordination process with tetrazine ring occurs.

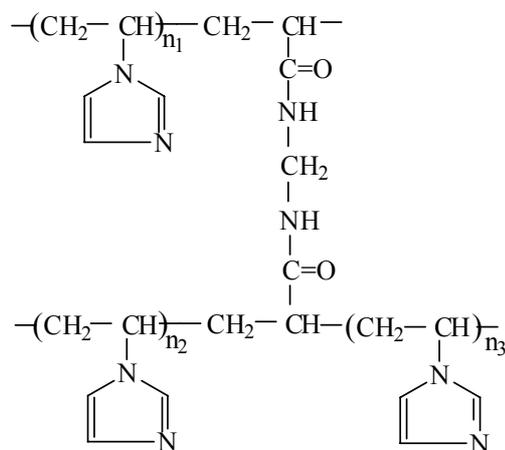
Weak base anion exchangers as beads were obtained by aqueous suspension polymerization of N-vinylimidazole with divinylbenzene,³⁶ according to Scheme 4.



Scheme 4. Chemical structure of some imidazole weak base anion exchanger.

This ion exchanger has high retention capacities for polar compounds from their aqueous solutions due to its high polarity and aromatic character. The latter peculiarity is responsible for the π - π interactions between sorbent and pollutants.

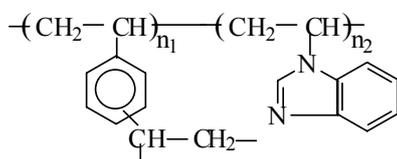
For the crosslinked N-vinylimidazole : N, N' - methylenebisacrylamide copolymer, with chemical structure according to Scheme 5, the retention property of Hg(II) from its acid aqueous solutions was investigated.³⁷



Scheme 5. Chemical structure of a N-vinylimidazole: N, N' - methylenebisacrylamide copolymer.

The vinylimidazole rings showed a higher affinity for Hg(II) cation at pH=2 due to H₂SO₄ compared to that due to HCl. The ability to bind of Hg(II) cations depends mostly on pH and less on temperature and counterion of the Hg(II) cation.

For the copolymer of N-vinylbenzimidazole: divinylbenzene (Scheme 6) with a weak base exchange capacity of 2.4 meq.g⁻¹ and pK_b=8.3 was analysed the retention property of platinum group metals and gold as their chlorocomplexes.³⁸



Scheme 6. Chemical structure of a N-vinylbenzimidazole: divinylbenzene copolymer.

The immobilization of N-methyl-D-glucamine on a vinylbenzyl chloride: divinylbenzene copolymer beads, according to Scheme 7, yields an effective and selective sorbent for arsenate ions³⁹

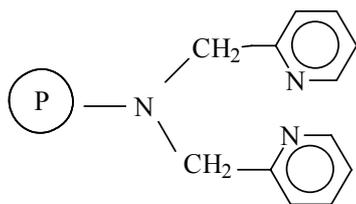
The ion exchange from Scheme 9 contains both amine groups and sorbitol moieties.

Arsenic which is a very toxic element exists mainly as arsenate [As(V)] and arsenite [As(III)] in grounded water. In the typical pH range of the water in the environment As(V) can be removed by ion exchange process, but As(III) can not removed by this process because it is present as un-ionized form H₃AsO₃. For this, a preoxidation step to convert arsenite to arsenate is needed. The results indicate that arsenate selectivity is dependent of immobilization degree with N-methyl-D-glucamine of the copolymer and the amine group must be in the protonated form. A study on the reaction between polyols and arsenate has shown that sorbitol forms a stable complex with As(V) in acid media whereas this complex decomposes in neutral medium.

This structure shown in Scheme 9 is also used for the removal of the boron. The presence of boron ions, even in small concentrations, can give rise to serious problems, as an example is for the water used in agricultural and horticultural applications.^{40, 41}

This ion exchanger complexed with ruthenium (III) is a catalyst with performance in the epoxidation of olefine as : cis – cyclooctene, cyclohexene and styrene.

Weak base anion exchangers which contain pyridine-nitrogen atoms and amine-nitrogen atoms (Scheme 11) can complex with Cu(II) cation and these complexes are with very high affinity for phosphate, arsenate and ionizable organic contaminants such as 2,4,6-trichlorophenol.⁴⁷

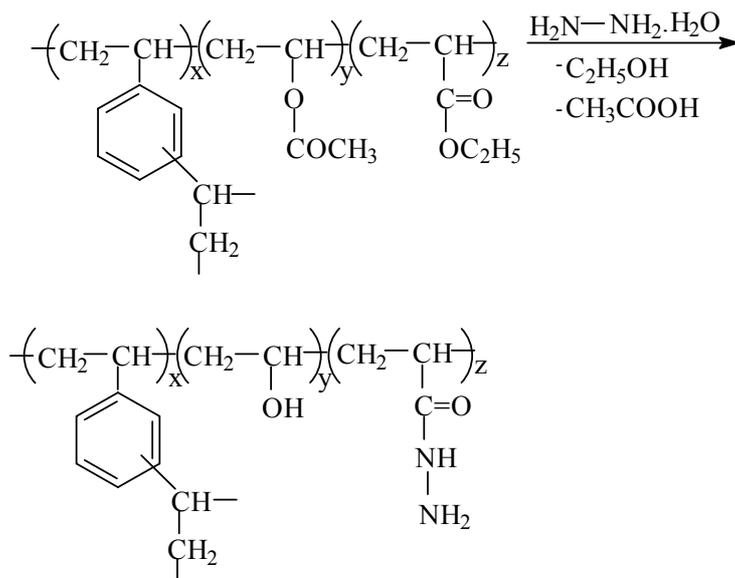


Scheme 11. Chemical structure of a repeat unit from an ion exchanger which contains pyridine – nitrogen atoms and an amine – nitrogen atom.

Magnetic weak base anion exchangers for the retention of heavy metal cation is a new trend in the achievement of sorbents for inorganic contaminants from wastewater. As an example: the matrix of glycidylmethacrylate:divinylbenzene containing statistically distributed maghemite nano crystals was functionalized to possess anionic groups.⁴⁸ Another example is due to fibrous weak base anion exchangers impregnated with nanoparticles of hydrated ferric oxide which they are selective sorbents for As(III) and As(V) species from aqueous solutions.⁴⁹

Weak base anion exchangers with high values of the ion exchange capacities due to hydrazide groups were performed from aminolysis reaction of some ethyl acrylate: vinyl acetate: divinylbenzene copolymers with $\text{H}_2\text{N}-\text{NH}_2 \cdot \text{H}_2\text{O}$, according to Scheme 12.⁵⁰

This type of exchanger has good values for the immobilization yields of the aminoacylase at pH 3.0.



Scheme 12. Chemical reaction of an ethyl acrylate: vinyl acetate: divinylbenzene copolymer with hydrazine hydrate.

CONCLUSIONS

Organic weak base anion exchangers are organic three-dimensional covalent networks, so-called matrices, which contain primary, secondary and/or tertiary amine groups.

They can be chemically modified natural products or synthetic products. The latter have a greater importance than those from a natural organic source and have found much wider technical applications because of their higher chemical stability and mechanical strength as well

as their very different physical and chemical structures.

Weak base anion exchangers act as ion exchangers in the strong acid media where the amine groups are protonated. In fact, these ion exchangers are sorbents for strong acids and polymeric ligands for heavy metal cations.

The most common and commercially available weak base resins are those which contain dimethylamino or polyethylenamino groups attached to styrenic or acrylic – type matrices as bead shapes.

This paper, besides the peculiarities of the weak base resins, shows the synthesis of new matrices with regard to their chemical structures and shapes as well as adds compounds into them such as magnetic matrices. The paper also depicts different chemical structures of the amine moieties. The more special applications of the presented weak base resins are also mentioned.

REFERENCES

1. F. Helfferich "Ion Exchange", McGraw-Hill, New York, 1962.
2. O. Samuelson, "Ion Exchange Separations in Analytical Chemistry", John Wiley, New York, 1963.
3. R.L. Albright and P.A. Yarnell "Ion-exchange polymers: Encyclopedia of Polymer Science and Engineering", John Wiley, New York, 1987, 2nd edn., vol.8.
4. Streat M. Naden D, (eds) "Ion exchange and Sorption Processes in Hydrometallurgy. Critical Reports on Applied Chemistry", John Wiley, New York, 1987, ch. 3 and 4, vol.15.
5. K. Dorfner, "Ion exchangers", Ann Arbor Science Publishers, Michigan, 1972, 3rd edn.
6. K. Dorfner (Ed), "Ion exchangers", W. de G. de Gruyter, Berlin, 1991.
7. J. A. Mikes and L. I. Kovacs, *J. Polym. Sci.* **1962**, *59*, 209-214.
8. P. N. Nesterenko and P. R. Haddad, *Analytical Sci.* June **2000**, *16*, 565-574.
9. M. J. Hudson, "Coordination chemistry of selective ion exchange resins", Ion Exchange, Science, and Technology, NATO ASI Series. Boston, 1986, p.35-66.
10. Y. Kaeamura, M. Mitsuhashi and H. Tanibe, *I&EC Res.*, **1993**, *32*, 386-391.
11. W. H. Holl, *Vom Wasser*, **1997**, *89*, 13-24.
12. C. D. Vlad, C. Luca, I. Petrariu and A. Carpov, *Mat. Plast.*, **1978**, *15*, 75-79.
13. C. P. Gomes, M. F. Almeida and J. M. Loureiro, *Sep. Purific. Technol.*, **2001**, *24*, 35-57.
14. B. Bolto, D. Dixon, R. Eldridge, S. King and K. Linge, *Water Research*, **2002**, *36*, 5057-5065.
15. S. Maxim, A. Flondor, I. Bunia and C. Luca, *Eur. Polym. J.*, **1998**, *34*, 1379-1385.
16. I. Bunia, C. N. Cascaval, D. Rosu, C. Ciobanu and M. Popa, *Polym. Degrad. Stab.*, **2000**, *70*, 205-215.
17. V. Neagu and I. Bunia, *Polym. Degrad. Stab.*, **2004**, *83*, 133-138.
18. S. Maxim, A. Flondor, I. Bunia, C. Luca, I. Rabia, J. Zerouk, F. Iayaadene and H. Guettaf, *J. Appl. Polym. Sci.*, **1999**, *72*, 1387-21394.
19. C. Luca, C. Maruta, I. Bunia, A. M. Urmenyi, M. Sandu and D. Rata, *J. Appl. Polym. Sci.*, **2005**, *97*, 939-938.
20. A. Barsanescu, R. Buhaceanu, V. Dulman, I. Bunia and V. Neagu, *J. Appl. Polym. Sci.*, **2004**, *93*, 803-808.
21. I. Bunia, M. Popa, F. Matei and G. Ionescu, *Rev. Chim. Bucharest*, **2002**, *53*, 198-202.
22. R. Buhaceanu, V. Dulma and I. Bunia, *Analele St. Univ. "Al.I.Cuza" Iasi, seria Chimie*, **2001**, *IX*, 67-72.
23. A. Barsanescu, R. Buhaceanu, V. Dulma and I. Bunia, *Analele St. Univ. "Al.I.Cuza" Iasi, seria Chimie*, **2001**, *IX*, 61-66.
24. A. A. Shunkevich, Z. I. Akulich, G. V. Mediak and V. S. Soldatov, *React. Funct. Polym.*, **2005**, *63*, 27-34.
25. C. Luca and S. Dragan, - unpublished data.
26. S. Dragan, M. V. Dinu and C. D. Vlad, *J. Appl. Polym. Sci.*, **2003**, *89*, 2701-2707.
27. C. D. Vlad, M. V. Dinu and S. Dragan, *Polym. Degrad. Stab.*, **2003**, *79*, 153-159.
28. M. A. Malik, R. Mukhtar, S.A.R. Zaidi, S.Ahmed and M.A. Awan, *React Funct. Polym.*, **2002**, *51*, 117-120.
29. R. Mukhtar and S. A. R. Zaidi, *The Nucleus*, **1997**, *34*, 85-87.
30. M. Chanda and G. R. Rempel, *React. Polym.*, **1992**, *17*, 159-174.
31. M. Chanda and G. R. Rempel, *React. Polym.*, **1992**, *18*, 141-154.
32. S. F. Marsh, *Solv. Extract. Ion Exch.* **1989**, *7*, 889-908.
33. C. T. L. Luz, F. M. B. Coutinho, *J. Appl. Polym. Sci.*, **2004**, *91*, 66-669.
34. N. Fontanals, R. M. Marce, M. Galia, F. Borrull, *J. Polym. Sci., Part A: Polymer. Chem.*, **2003**, *41*, 1927-1933.
35. K. D. Topp, M. Grote, *React. Funct. Polym.*, **1996**, *31*, 117-136.
36. N. Fontanals, R.M. Marce, M. Galia and F. Borrull, *J. Polym. Sci., Part A, Polym. Chem.*, **2004**, *42*, 2919-2025.
37. M.J. Molina, M. R. Gomez-Anton, B. L. Rivas, H. A. Maturana, and I. F. Pierola, *J. Appl. Polym. Sci.*, **2001**, *79*, 1467-1475.
38. G.V. Myasoedova, N. I. Shcherbinina, E. A. Zakhartchenko, S. S. Kolobov, L. V. Lileeva, P. N. Komozin, I. N. Marov and V. K. Beliyeva, *Solv. Extract. Ion Exch.*, **1997**, *15*, 1107-1118.
39. L. Dambies, R. Salinaro and S. D. Alexandratos, *Environ. Sci. Technol.*, **2004**, *38*, 6139-6146.
40. M. Badruk, N. Kabay, M. Demircioglu, H. Mordogan and U. Ipkoglu, *Separation Sci. Techn.*, **1999**, *34*, 2981-2995.
41. M. Badruk, International Geothermal Conference, Reykjavik, Sept. 2003; session 14; S14, paper 019, p.8-13.
42. D. J. Bartkowiak and B. N. Kolarz, *Eur. Polym. J.*, **2002**, *38*, 2239-2246.
43. H. Egawa, M. Nakayama, T. Nonaka, H. Yamamoto and K. Uemura, *J. Appl. Polym. Sci.*, **1987**, *34*, 1557-1575.
44. F. M. B. Coutinho, S. M. Rezende and C. C R Barbosa, *React. Funct. Polym.* **2001**, *49*, 235-248.
45. V. Neagu, I. Bunia, I. Plesca and M. Popa, *J. Appl. Polym. Sci.*, **2003**, *88*, 2956-2962.
46. R. Antony, G. L. Tembe, M. Ravindranathan and R. N. Ram, *Eur. Polym. J.*, **2000**, *36*, 1579-1589.
47. W. D. Henry, D. Zahao, A. K. SenGupta and C. Lange, *React. Funct. Polym.*, **2004**, *60*, 109-120.
48. T. Dahlke, Y H Chen, M. Franzreb and W H Holl, *React. Funct. Polym.*, **2006**, *6*, 1062-1072.
49. O. M. Vatutsina, V. S. Soldatov, V. I. Sokolova, J. Johann and M. Bissen, A. Weissenbacher, *React. Funct. Polym.*, **2007**, *76*, 184-201.
50. I. Bunia, V. Neagu and C. Luca, *React. Funct. Polym.*, **2006**, *66*, 871-883.

