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Adsorption studies of some inorganic and organic salts on new zwitterionic ion exchangers with carboxybetaine moieties

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ABSTRACT

The synthesis and characterization of two structures of crosslinked polyzwitterionic carboxybetaines based on the 4-vinylpyridine: divinylbenzene macromolecular supports of gel and porous type as well as the evaluation of their retention property of organic and inorganic salts are reported. Ion exchange capacity values, pK_a, FT-IR spectroscopy and ESEM images of their polymeric precursors proved the content of ionic groups, the selectivity for hydrogen atom and the morphology structure of the zwitterionic ion exchangers with positive and negative charges located in the same structural unit and bound by one or two methylene groups.

The yielded compounds exhibited retention capacities for divalent and trivalent heavy metals as well as for cefotaxime from aqueous solutions. The values are related to their chemical and morphological structures. The highest retention capacity values of the heavy metals and cefotaxime were obtained when the zwitterionic ion exchanger with two methylene groups as the spacer between the opposite charges and porous structures was used in the investigation studies.

1. Introduction

Zwitterionic polymers in which the anionic and cationic groups are linearly arrayed on the pendant side chain of the molecular backbone have attracted attention in the last years due to their unique structures and excellent properties [1,2]. Particularly, zwitterionic ion exchangers are synthetic insoluble crosslinked macromolecules carrying ionic active groups, both the positive and negative charges in the same structural unit. There are the following types of the zwitterionic ion exchangers: (i) polyampholytes resins having a continuous distribution of oppositely charged group; (ii) ion exchangers in which there are oppositely charged groups along or pendant to the polymeric chain. The idea to combine both anion and cation groups in a single particle of an ion exchanger was to improve the ion exchange selectivity.

The evolution of zwitterionic ion exchangers had several steps depending on the distribution of the ionic groups according to the literature [3]. Many traditional polyampholyte ion exchangers with alternating sequences of cation and anion exchange groups have been synthesized and are interested in recent years in relation to the development of polysulfones and polycarboxybetaines [4–6].

The agglomerated ion exchangers were proposed for the first time by Small et al. and are based on the inert core of sulfonated styrene: divinylbenzene copolymer coated with a monolayer of electrostatically bound anion exchange microbeads of latex [7]. The outstanding characteristics of these agglomerated ion exchangers are their chromatographic performance and excellent chemical stability over the entire pH range [8–11].

Another approach to the synthesis of zwitterionic ion exchangers was proposed by Dolgonosov et al. when treated small particles of macroporous strong base anion exchanger based on styrene: divinylbenzene copolymer with sulfuric acid of different concentrations [12,13].

The most effective way to realize the advantage of zwitterionic ion exchangers is to combine the oppositely charged functional groups in one molecule which is immobilized onto the stationary phase [14–25].

An interesting approach for modeling the interaction of polar organic molecules with phospholipids membranes called immobilized artificial membrane chromatography was proposed by Pidgeon et al. [23–30]. These materials have a number of desirable features such as, the reduced shrinking, improved mechanical stability, superior mass transfer characteristics of the surface, unique separation selectivity, often simultaneous separation of anions and cations with a single column and the improvement of the detection sensitivity.

A major class of these compounds is zwitterionic polymers with betaine structures where the opposite charges are located in the same repeat unit with an alkylene group between them. The positive charge is due to a quaternary ammonium group whereas the anionic charge may be due to either carboxylate group: (carboxybetaines/carbobetaines), sulfonate groups (sulfobetaine)

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or phosphonate/phosphate/phosphinate grouping (phosphobetaines) [31].

According to the recent literature various novel approaches have been designed to prepare zwitterionic organic polymers. These methods include the ring opening of haloalkysulfonates [22,32,33], the copolymerization between zwitterionic monomers via free radical polymerization [34,35], living free radical polymerization [36], aqueous polymerization [37] or by suitable polymer-analogous reactions performed on the vinylic polymers [38,39].

In order to perform zwitterionic polymer materials with high selectivity as a result of simultaneous interactions of the positive and negative charges with both functional groups we present for the first time the achievement of crosslinked zwitterionic ion exchangers. The work was focused on the synthesis of zwitterionic ion exchangers with ammonium and carboxylate groups separated by a spacer of one and two methylene groups and arrayed on the pendant chain of the crosslinked 4-vinylpyridine: divinylbenzene copolymer of gel and porous types.

The adsorption properties of the yielded zwitterionic ion exchangers towards heavy metals and alkaline earth metals as well as cefotaxime sodium salt were studied by batch method under non-competitive conditions. The investigated parameters that influence the retention were the initial concentration of analytes, contact time and counter ions type.

2. Experimental

2.1. Materials

4-Vinylpyridine (4-VP) supplied from Fluka was purified by vacuum distillation immediately before to use. Divinylbenzene (DVB) supplied from Fluka was a technical mixture of isomers ~80% (GC) with the residual mainly 3- and 4-ethylvinylbenzene.

The initiator (1.5 wt%), benzoyl peroxide and diluent, toluene are of analytical grade and were used as received. In the polymerization process, the aqueous phase contains a polymeric stabilizer (0.5 wt%) prepared by hydrolysis with aqueous NH_3 solution of poly(styrene-co-maleic anhydride), gelatine (0.12 wt%) and NaCl (3 wt%).

Sodium chloroacetate (98%) was supplied from Aldrich Chem. Co. and used as received. Acrylic acid (AA) was purified by distillation under reduced pressure before used.

Stock solutions (1000 mg L^{-1}) of Fe(III), Al(III), Ni(II), Zn(II), Pb(II), K(I) and Na(I) were prepared by dissolving of their appropriate amounts of analytical reagents grade in double distilled water. The working metal solutions were prepared by adequate dilution.

Cefotaxime sodium salt (CF) was purchased from Fluka Chemical Co. and used as received. The working solutions have the concentrations in the range of 70 and 3000 mg L^{-1}.

1N HCl and 1N NaOH solutions of known concentrations were used to determine the ion exchange capacity and pK_a values.

2.2. Methods

2.2.1. Synthesis of 4-VP:DVB copolymer

4-VP:DVB copolymers of gel and porous type were obtained by free radical suspension polymerization in water of the corresponding monovinylic monomer with DVB as crosslinking agent according to literature [40]. When toluene was used as diluent throughout this study, its content (D) was calculated as follows: D = [mL diluent/(mL diluent + mL monomers)].

Morphological characteristics of the copolymers are determined: real density (ρ_r) was measured in n-heptane; apparent density (ρ_{ap}) by picnometry at a residual pressure of about 10^{-3} mm Hg; cyclohexane, methanol and water uptakes (respectively, Q_{Ch}, Q_T and Q_W) by centrifugation method.

2.2.2. Synthesis of zwitterionic ion exchangers

Zwitterionic ion exchangers with carboxybetaine moieties were prepared by the betainization reaction of the 4-VP:DVB copolymers of gel and porous type with sodium chloroacetate and acrylic acid. Thus, 10 g copolymers were swollen in 50 mL methanol for 24 h at room temperature and then the betainization reagents dissolved in water to produce a solution of 20% (w/v) concentration were added. Amount of reagent was calculated for a nitrogen:reagent molar ratio of 1:1.2.

The reaction mixture was kept under gentle stirring at 60 °C for 120 h. Afterwards the compounds yielded from the reaction with sodium chloroacetate were recovered by filtration and washed with deionized water until the absence of Cl^- in the effluent which indicated the removal of sodium salt. The beads synthesized by the betainization reaction with acrylic acid were filtered and treated with 1 mol L^{-1} HCl and then washed with deionized water until no chloride ions were present in the effluent, followed by the treatment with 0.5 mol L^{-1} Na_2CO_3 solution and finally washed with deionized water until the effluent had the neutral pH.

The beads of zwitterionic ion exchangers with carboxybetaine structure were sieved to a particle size of 0.3–0.6 mm diameter and characterized by the degrees of betainization using FT-IR spectroscopy.

Both morphological types of the yielded compounds were characterized by the following features: the volume weight (W_v, expressed as g mL^{-1}), anionic or cationic weight exchange capacity, mequiv g^{-1}; anionic or cationic volume exchange capacity (C_v), mequiv mL^{-1} wet product; the water uptake capacity (Q_{Wt}) of the complete hydrated ion exchanger samples expressed as g water g^{-1} dry ion exchanger.

Anion exchange capacity (AEC) expressed as mequiv mL^{-1} was determined according to the following method: a known volume of the ion exchange resin was treated with a specific volume of 1N HCl solution of known concentration and the excess of hydrochloric acid was removed by passing through the resin the mixture solution of water:methanol 1:2 (v/v). The eluent was measured by titration to the mixed indicator end point with 1N NaOH solution.

C_v was calculated according to Eq. (1):

$$C_v = \frac{V_1 f_1 - V_2 f_2}{V} \tag{1}$$

where V_1 is the volume of 1N HCl solution, mL; V_2 is the volume of 1N NaOH, mL; V is the volume of resin, mL; f_1 is the factor of 1N HCl solution; f_2 is the factor of 1N NaOH solution.

C_{Wt} was determined by drying of the known volume of the ion exchangers at 110 °C up to constant weight and was calculated by Eq. (2):

$$C_{Wt} = \frac{V_1 f_1 - V_2 f_2}{m} \tag{2}$$

where V_1, V_2, f_1 and f_2 have the same meaning as in above equation and m is the weight of the resin, g.

Cation exchange capacity (CEC) was determined using the Mohr method when the cation exchange capacity was determined by converting ionic groups to the Na^+ ionic form by back-titration with 0.01 mol L^{-1} HCl [41].

2.2.3. Determination of the retention capacity of inorganic and organic salts

After air drying the ion exchangers were stored for the sorption experimental studies by batch method. 0.1 g ion exchangers of known humidity was contacted with 25 mL aqueous solution of inorganic and organic salts of various concentrations at room temperature in the glass-stopped Erlenmeyer flasks. The samples were shaken for the desired contact times. In all experiments the samples were separated by filtration and the filtrate was analyzed by