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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

AAS spectrometry for metal content and UV–vis spectrometry for cefotaxime content. The amount of the counter-ions of metals was measured by ionic chromatography.

The concentrations of the organic and inorganic compounds were calculated from the concentration of analytes in the aqueous solution before and after equilibration adsorption from the weight of the dry samples used using Eq. (3):

$$Q = \frac{(C_i - C_f)V}{m} \tag{3}$$

where Q is the retained amount, mg g^{-1}; C_i, and C_f are initial and final concentrations of the analytes (mg mL^{-1}); V is the volume of the solution (mL) and m is the dry weight of the beads (g).

Kinetic analysis is required to obtain an insight of the rate of adsorption and the rate limiting step of the transport mechanism, which are primarily used in the modeling. To determine the kinetics of adsorption, a pseudo-second-order model was used [42]:

$$\frac{dq_t}{dt} = k_s(q_e - q_t)^2 \tag{4}$$

where k_s is the rate constant for pseudo-second-order adsorption (g mg^{-1} min^{-1}); q_e is the amount of analyte adsorbed (mg g^{-1}) at equilibrium defined as $(C_0 - C_e)V/W q_t$; q_t is the amount of analyte adsorbed at any time; C_0 is the initial analyte concentration (mg L^{-1}), C_e is the equilibrium analyte concentration (mg L^{-1}); V is the volume of analyte solution used for the adsorption (L); W is the weight of the adsorbent used (g).

By solving Eq. (4) with the initial condition $q_t = 0$ at $t = 0$:

$$\frac{t}{q_t} = \frac{1}{k_s q_e^2} + \frac{1}{q_e} t \tag{5}$$

The values of the pseudo-second-order rate constant, k_s and the equilibrium analyte uptake, q_e can be obtained from the slope and intercepts of the plot t/q_t with time, t. This pseudo-second-order rate model was observed to be valid for all the metal adsorption experiments.

The approaching equilibrium factor (R_W) which represents the characteristics of kinetic curve of an adsorption system is given by [43]:

$$R_W = \frac{1}{1 + k_s q_e t_{ref}} \tag{6}$$

where t_{ref} is the longest operation time of kinetic experiments. The adsorption curve is called approaching equilibrium when R_W is in the range $0.1 < R_W < 1$; and it is well approaching equilibrium when R_W is in the range $0.1 < R_W < 0.01$ and it is drastically approaching equilibrium when $R_W < 0.01$.

2.3. Instrumentation

Atomic absorption spectrometry (Analyst 200, PerkinElmer) was used for the heavy metals analysis. Alkaline earth elements as well as the metal counter-ions were analyzed by Ionene Chromatographie–DIONEX DX 500, Varian SpectrAA-220-FS.

A shaker with thermostat M00/M01 Memmert GmbH model was used for the adsorption experiments.

Infrared spectra were recorded as KBr pellets using a Bruker Vertex 70 FT-IR spectrometer collecting 124-scans with a resolution of 2 cm^{-1}.

Water uptake is defined as the amount of water absorbed by 0.1 g of ion exchanger. It is measured taking the dried resin in neutral ionic form. The dried ion exchangers were contacted with distilled water for 24 h, then centrifuged at 2000 rpm for 20 min and finally weight.

The ESEM studies were performed on samples fixed on copper supports. The surface was examined by using an environmental scanning electron microscope type Quanta 200 at 400 and 2000 magnification operating at 30 kV with secondary electrons in low vacuum. The Quanta 200 microscope is equipped with an energy dispersive X-ray system for qualitative and quantitative analysis and elemental mapping.

Cefotaxime amount was analyzed by UV–vis SPEKOL 1300 spectrophotometer (Analytik Jena) at $\lambda = 236$ nm.

3. Results and discussion

3.1. Synthesis and characterization of zwitterionic ion exchangers with carboxybetaine moieties

4-VP:DVB copolymers with two morphological structures were prepared as substrates for the synthesis of zwitterionic ion exchangers with carboxybetaine structure. The copolymers were characterized by nitrogen content determined by elemental analysis and those with a content of 11.5% nitrogen for gel and 9.5% nitrogen for porous type were used for the subsequent chemical transformations.

The characteristic values of the apparent density and uptake coefficient in various solvents as well as their internal structures are presented in Table 1 and Fig. 1.

The following conclusion could be drawn from Table 1 and Fig. 1: C1 copolymer has a gel morphology whereas C2 copolymer has a porous one. This affirmation is evidenced by the values of apparent density, cyclohexane uptake coefficients (0.018 and 0.301 mL g^{-1}, respectively) as well as the SEM micrographs [44,45]. Q_{Ch} values satisfy Millar's rule, which states that porosity exists only when $Q_{Ch} > 0.1$ mL g^{-1}. Also, SEM image of C2 copolymer showed a texture composed by agglomeration of microspheres. Also, both copolymers exhibited the highest uptake coefficients for methanol and therefore, methanol was used as reaction medium for the further chemical transformations.

The method for preparing the zwitterionic ion exchangers incorporating the carboxybetaine moieties into pyridine copolymer is shown schematically in Scheme 1.

According to Scheme 1, the betainization reactions on the 4-VP:DVB copolymers were performed by the quaternization of the copolymers with a salt of a halogen alkylene carboxylic acid namely, sodium chloroacetate followed by the removal of NaCl and nucleophilic addition of pyridine copolymers to carbon–carbon double bond of acrylic acid.

The yielded compounds were characterized by FT-IR spectroscopy. For illustration Fig. 2 presents the FT-IR spectra of the C copolymer of gel type and the products prepared by both betainiza-

Table 1
Physicochemical characteristics values of 4-VP:DVB copolymers.

Sample code	DVB (wt%)	Diluent (D)	ρ_{ap} (g mL^{-1})	N (%)		Q (mL g^{-1})		
				Theoretic	Found	Q_{Ch}	Q_M	Q_W
C1[a]	8	–	1.080	11.47	11.00	0.018	1.96	1.32
C2	10	Toluene (D = 0.2)	0.851	10.51	9.94	0.301	1.75	0.83

[a] $\rho_r = 1.085$ g mL^{-1}.

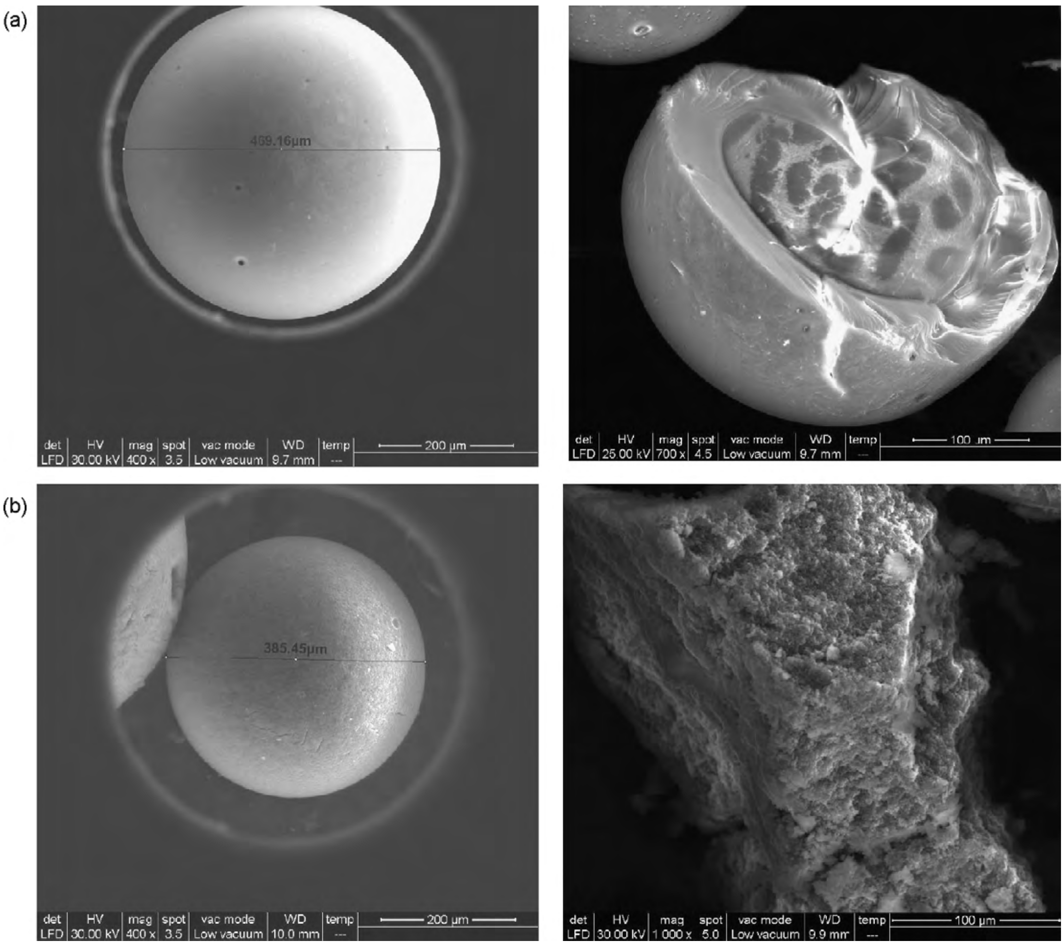


Fig. 1. SEM images of the beads cross-section of C1 (a) and C2 (b) samples.

tion reactions. From the spectra presented in Fig. 2 the following aspects are evidenced: in the spectrum (B) a rather broad band with maximum at 1643 cm^{-1} is observed. This band shows two major spectral contributions, one due to the stretching vibration of the pyridinium cation at 1643 cm^{-1} is attributable to antisymmetric stretching of carboxylate groups [45–47]. It should be noted that the intensity of the υ_{as} COO^- band is the fact higher than that of the pyridinium ring vibration. According to the intensity rule the intensities of the components are additive and the pyridinium stretching vibration appears more intense than υ_{as} COO^-.

The spectrum of ZIE II (C) shows characteristic carboxylate group vibrations. The band at 1642 cm^{-1} is associated with the stretching of betainized pyridinium rings. The peak at 1587 cm^{-1} is characteristic of antisymmetric stretching vibration of carboxylate groups when the spacer between the two opposite charges contains two methylene groups. The symmetric stretching vibration of COO^- appears at 1395 cm^{-1}. The degree of betainization of ZIE II is about 94%.

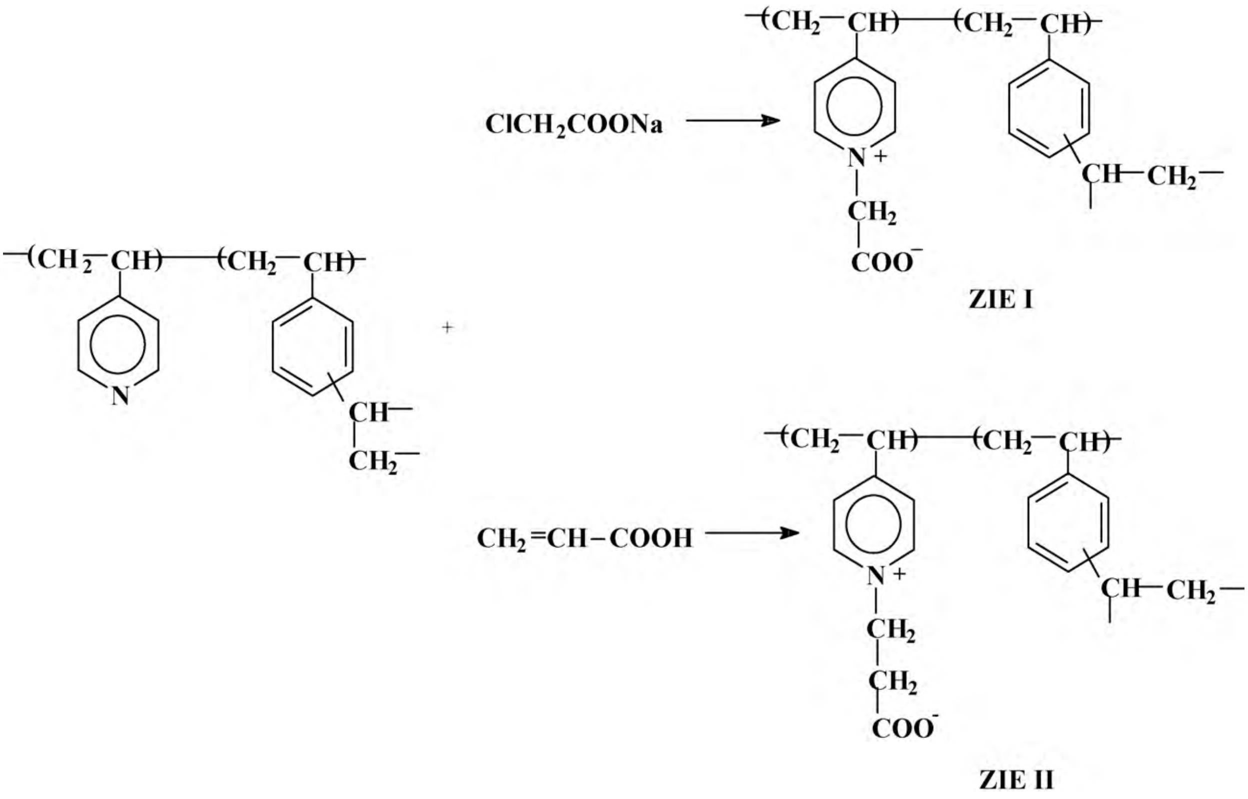
The degree of betainization was estimated from the relative ratio of the integrated area of the absorptions of betainized (1643 cm^{-1}) to "free" (chemically unmodified) pyridine rings (1598 cm^{-1}). Individual peaks were obtained by curve-fitting the spectrum in region 1790–1530 cm^{-1} into Gaussian components using the Levenberg–Marquardt method. The IR peaks were integrated with OPUS software using curve-fitting of the adsorption peaks. The calibration curve was obtained by linear least square regression with $R = 0.95472$. The degree of betainization of ZIE I.1 with gel structure is about 90% whereas of ZIE II.2 of porous type is about 98%.

It is commonly recognized that potentiometric titration is one of the most important methods for investigation and characterization of ion exchangers. The acid–base properties of ion exchangers are characterized by the affinity of their functional groups to H^+ or HO^-.

Table 2
Characteristics of the zwitterionic ion exchangers.

Sample code[a]	Anion exchange capacity		Cation exchange capacity		g_ν (g mL^{-1})	Q_W (mL g^{-1})
	C_{Wt} (mequiv g^{-1})	C_V (mequiv g^{-1})	C_{Wt} (mequiv g^{-1})	C_V (mequiv g^{-1})		
ZIE I.1	2.61	1.20	2.55	1.17	0.4587	0.95
ZIE I.2	2.73	0.89	1.64	0.86	0.3260	0.70
ZIE II.1	2.48	1.42	2.39	1.37	0.5713	1.51
ZIE II.2	2.88	1.17	2.79	1.13	0.4051	1.05

[a] ZIE I.1 and ZIE II.1 are zwitterionic ion exchangers with the morphology of gel type; ZIE I.2 and ZIE II.2 are zwitterionic ion exchangers with the morphology of porous type.



Scheme 1. Synthetic strategy of the zwitterionic ion exchangers with carboxybetaine moieties.

The degree of ionization of the ionogenic groups depends on the acid or base strength of the groups, i.e., on their p*K* and pH values. The electrostatic interactions play also a key role in the determination of the pK_a values of the acid and basic groups. Weakly acid and basic groups are of particular importance because the charge balance can be controlled by the pH and salt concentration of the external solution [48].

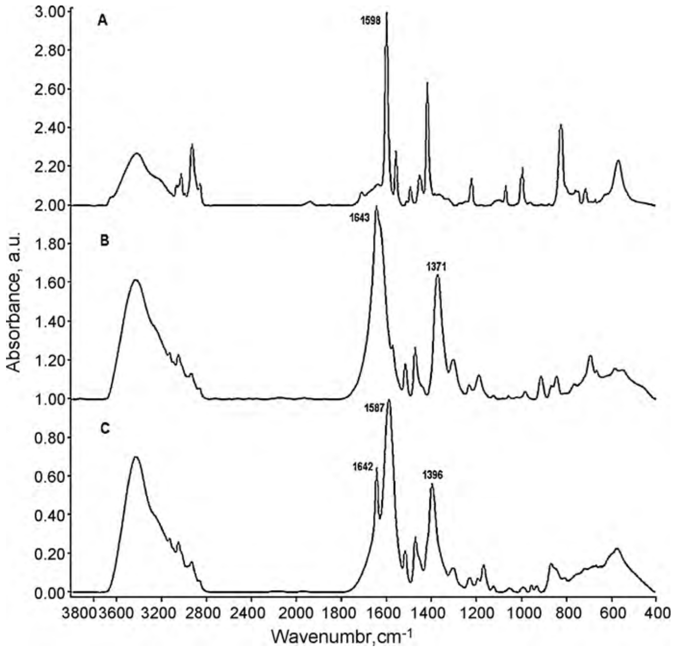


Fig. 2. FT-IR spectra of unmodified (A) and functionalized C1 copolymer with sodium chloroacetate (B) and acrylic acid (C).

In order to verify the chemical stability the yielded compounds were treated with 1 mol L^{-1} HCl and then washed with deionized water until no chloride ions were presented 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 washing water was neutral. The chemical stability of the zwitterionic ion exchangers was confirmed by FT-IR spectroscopy when the resins with the same degrees of betainization as the initial resin were obtained.

In the process of titration a suspension of the ion exchanger in the solution the pH is measured in the solution and the ion exchanger plays the role of a stock of ions H^+ or HO^- consumed in the reaction with the titrant.

In order to characterize acidic strength of the zwitterionic ion exchangers synthesized in the present paper the pK_a has been calculated by titration with 1N HCl solution. The amount of the aqueous phase of the titrant portion was measured by weight with precision 0.0002 g. The internal between additions of the titrant portions was 20 min. The glass electrode was additionally calibrated in the presence of 1 M KCl in the pH range of 1.5–12.6. It is already known that the weak acid group has a pK_a value in the approximate range −2 to 12 in water. The calculated pK_a value is 2.62 for both ion exchangers and therefore, it can affirm that these ion exchangers with carboxybetaine structure exhibited the selectivity to hydrogen ion.

Characteristics of the zwitterionic ion exchangers prepared according to Scheme 1 showed good values of the exchange capacity values, lower values for the water retained capacity than that of the precursors copolymers as well as the porous ion exchanger is more hydrophobic than the gel one (Table 2).

3.2. Sorption studies of the inorganic and organic salts

Table 3 shows the retention capacity values (C_R) as mequiv metal cation per g dried resin and mequiv of anion per g dried resin,

Table 3
Retention capacity of inorganic salts for the zwitterionic ion exchangers with carboxybetaine moieties.

Inorganic salt		C_R (mequiv g^{-1})			
		ZIE I.1	ZIE I.2	ZIE II.1	ZIE II.2
$Fe(NO_3)_3$	Fe(III)	0.731	1.190	1.65	4.66
	NO_3^-	2.175	3.530	2.15	6.15
$Al(NO_3)_3$	Al(III)	1.660	4.700	0.805	7.06
	NO_3^-	4.297	13.650	2.405	21.18
$Ni(NO_3)_2$	Ni(II)	0.333	0.365	0.500	0.830
	NO_3^-	0.681	0.731	1.019	1.712
$Pb(NO_3)_2$	Pb(II)	0.218	0.302	0.280	0.400
	NO_3^-	0.431	0.642	0.523	0.795
$ZnSO_4$	Zn(II)	0.152	0.511	0.500	0.913
	SO_4^{2-}	0.138	0.503	0.480	0.895
KCl	K^+	0	0	0	0
	Cl^-	0	0	0	0
NaCl	Na^+	0	0	0	0
	Cl^-	0	0	0	0
Na_2SO_4	Na^+	0	0	0	0
	SO_4^{2-}	0	0	0	0

respectively, for both structures of zwitterionic ion exchangers with gel and porous structures. From the data presented in Table 3 it is evident that both types of zwitterionic ion exchangers synthesized in this work retained metal cations and anions from aqueous solutions except the case when the solutions of alkaline earth metals were used. It is also observed that the ion exchanger with porous structure exhibited higher retention capacity than that of gel type.

This result could be explained by the improvement of the access for cations and anions into the polymeric matrix which broken the electrostatical interaction between quaternary ammonium (+) and carboxylate groups (−). Zwitterionic ion exchangers with two methylene groups between the opposite charges showed higher values of the C_R than the ion exchangers with carboxybetaine moieties separated by one $-CH_2-$ group. This behaviour of the crosslinked polycarboxybetaines towards metal salts is due to the distance between the positive and negative charges and their chemical environment. In general, polycarboxybetaines might undergo partial protonation of the carboxylate groups in protic solvent such as, water leading to their transformation into corresponding cationic polyelectrolytes. Favorable distances between the quaternary ammonium and carboxylate groups allowed the formation of a very strong inner salt structures with uncommon behaviours for the zwitterionic ion exchangers, as in our case for ZIE I samples.

It is well-known that ion exchangers tend to prefer the ions of higher valence, smaller equivalent volume, greater polarizability, ions which interact more strongly with the fixed ionic groups. According to the Table 3 the order of the retention capacity values for both structures is the following: Al(III) > Fe(III) > Ni(II) > Pb(II) > Zn(II) [3,8,31].

Unlike the behaviour of the zwitterionic ion exchangers in the presence of heavy metals, different results have been performed when the solutions of alkaline earth metals were used. At the concentration of these elements of 500 mg L^{-1} no retention capacities were obtained. In contrast to the linear polybetaines which exhibited greatly enhanced solubility and extensive chain expansion in the presence of electrolyte [49,50], the crosslinked polybetaines are not capable of simultaneous interaction with both ions of added low molar mass electrolytes,

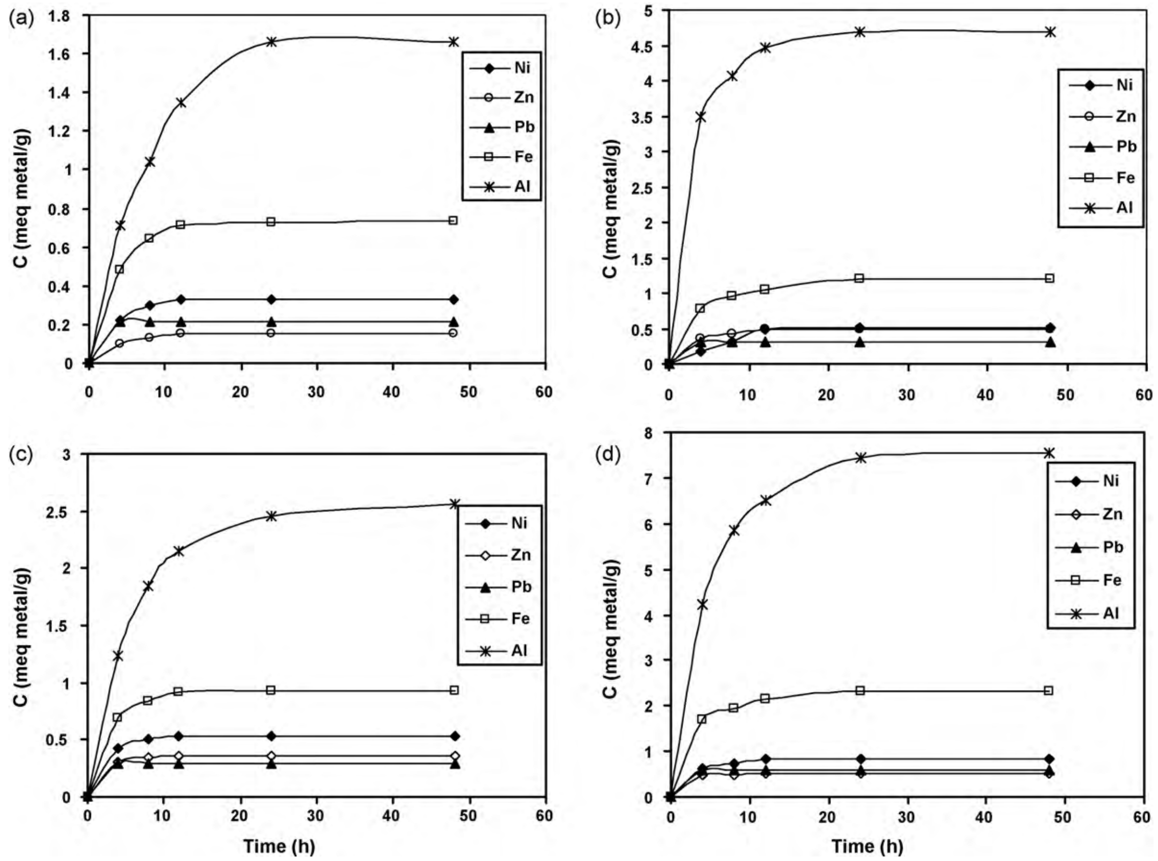


Fig. 3. Effect of the contact time on the retention capacity of various metals by ZIE I.1 (a); ZIE I.2 (b); ZIE II.1 (c); ZIE II.2 (d).

i.e., KCl, NaCl, Na_2SO_4 in the work conditions of the present study.

The crosslinked polyelectrolytes/metal-ion interaction can be only electrostatic in nature or can include the formation of coordinative bonds. The type of interaction depends on the chemical nature (ionization potential and electronic affinity) of the functional groups. The variables that affect the polyion/metal-ion interaction are classified into two groups: intrinsic to the polymer and extrinsic to the polymer. The former includes the polymer structure in terms of the composition and geometry, which affect the flexibility of the chains in solution, the branches of the chain, the chemical nature of the functional groups, their distribution at the polymer chain, and so forth. The second group includes the charge and type of the metal ion, the pH of the solution, the ionic strength, the temperature, and the dielectric constant of the medium.

The polymer/metal-ion interaction may be intramolecular, intermolecular, or both. The first is the most common for numerous groups of polymer–metal complexes showing comparatively high chemical and thermal stability. Another specific feature of these compounds is the total saturation of the coordination sphere of the transition-metal ion. The interchain polymer/metal-ion interaction may proceed via the binding of functional groups of two different macromolecules; usually one of them provides acidic functional groups, and the second provides basic groups. This type of metal-ion binding with mixed biopolymers is a process of great importance for biological reactions [51].

The effect of the contact time on the retention capacity for both zwitterionic ion exchangers is shown in Fig. 3.

For the concentration used in these experiments the retention capacities increased with time and reached the equilibrium in 12 h for the zwitterionic ion exchangers of porous type whereas the ion exchangers of gel type reached the equilibrium longer time, i.e., 24 h. High adsorption rates of the metals for the ion exchangers are observed at the onset and then plateau values are gradually reached in 12 h. The increasing contact time increased the metal retention capacities which remained constant after that the equilibrium reached in 12 h and 24 h for both structures of the ion exchangers [52].

The experimental data was fitted with linearized forms of pseudo-first order, pseudo-second order, Elovich and intra-particle diffusion model equations [53]. The result of the regression analysis (regression coefficient, $R^2 = 0.9989$) showed that adsorption on zwitterionic ion exchangers was best described by the pseudo-second-order equation, which showed higher correlation coefficients. The equilibrium capacities calculated from pseudo second-order model agreed closely with the capacities found from isotherm studies. Further, several other investigations determining the kinetics of adsorption onto crosslinked carboxybetaine compounds have also reported better correlations for the pseudo-second order model compared to other models [54]. Therefore, the kinetics was modeled using the equation for the pseudo-second-order model, given by Eq. (5).

Table 4
Pseudo-second-order sorption kinetics of heavy metals on zwitterionic ion exchangers: 500 mg L^{-1} metal solution (25 mL), 0.1 g adsorbent for all experiments.

Sample code	Metal	q_e (mequiv g^{-1})	k_s (g mg^{-1} h^{-1})	R_W
ZIE I.1	Ni(II)	0.333	0.06	0.0012
	Zn(II)	0.154	0.03	0.0031
	Pb(II)	0.218	0.04	0.0051
	Fe(III)	0.733	0.08	0.0041
	Al(III)	1.660	0.09	0.0064
ZIE I.2	Ni(II)	0.51	0.075	0.0044
	Zn(II)	0.50	0.07	0.0051
	Pb(II)	0.311	0.057	0.0087
	Fe(III)	1.19	0.07	0.0076
	Al(III)	4.70	0.09	0.0091
ZIE II.1	Ni(II)	0.533	0.06	0.0049
	Zn(II)	0.354	0.07	0.0056
	Pb(II)	0.292	0.056	0.0075
	Fe(III)	0.933	0.08	0.0048
	Al(III)	2.56	0.07	0.0074
ZIE II.2	Ni(II)	0.83	0.05	0.0056
	Zn(II)	0.535	0.46	0.0071
	Pb(II)	0.592	0.03	0.0058
	Fe(III)	2.33	0.07	0.0046
	Al(III)	7.56	0.08	0.0081

The values of q_e, k_s and R_W for the studied zwitterionic ion exchangers are shown in Table 4.

It is clear that the zwitterionic ion exchangers with a spacer of two methylene groups between opposite charges and porous structure exhibited higher adsorption capacity compared to that of a spacer of one methylene group and gel structure. The values of R_W indicate that the characteristic adsorption curve is drastically approaching equilibrium for most of the cases.

The effect of the type of the metal salts on the retention capacity is illustrated only for the nickel element (Fig. 4).

From Fig. 4 the following aspects have been observed: (i) ZIE 2 namely, the ion exchanger with porous structure exhibited the higher retention capacity values for Ni(II) than that with gel morphology; (ii) the highest values of nickel were retained from nitrate solution which has the highest constant stability in the aqueous solution; (iii) zwitterionic ion exchangers with a spacer of two $-CH_2-$ groups retained nickel from different salts in a higher amount than those with one methylene group between charges.

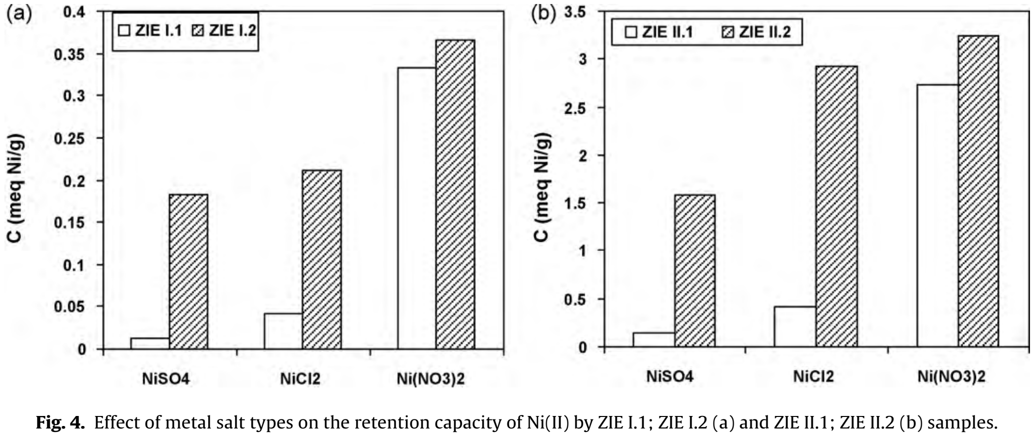


Fig. 4. Effect of metal salt types on the retention capacity of Ni(II) by ZIE I.1; ZIE I.2 (a) and ZIE II.1; ZIE II.2 (b) samples.

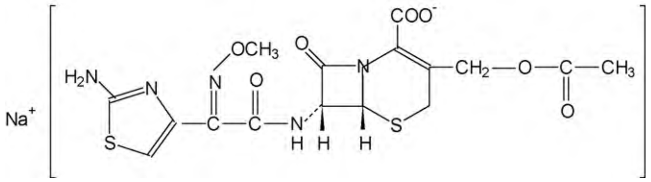


Fig. 5. Chemical structure of cefotaxime sodium salt.

Table 5
Retention capacity of cefotaxime sodium salt by zwitterionic ion exchangers.

Sample code	Concentration of CF ($g\,L^{-1}$)	C_R ($mg\,g^{-1}$)
ZIE I.2	7×10^{-2}	1.11
	7×10^{-1}	10.15
	15×10^{-1}	34.84
	30×10^{-1}	47.65
ZIE II.2	7×10^{-2}	1.375
	7×10^{-1}	22.64
	15×10^{-1}	47.55
	30×10^{-1}	57.23

The retention properties of the zwitterionic ion exchangers with carboxybetaine moieties were estimated by the retention capacity of the organic salt namely, cefotaxime sodium salt. Cefotaxime sodium salt is a drug which has the role to treat or prevent infections and its chemical structure is shown in Fig. 5.

The CF solution of different concentrations was loaded onto both structures of zwitterionic ion exchangers with gel and porous morphologies by batch method for different contact times. The results are presented in Table 5 and Fig. 6.

Effect of CF present initially in the aqueous solution was studied in order to asses the concentration range of CF which can be treated by these ion exchangers. As seen in Table 5 the retention capacity increased with the increasing of CF in the external aqueous solution for the studied concentration range in this work. It is obviously that the zwitterionic ion exchangers with carboxybetaine moieties retained bulky organic compounds at high concentration as well as the higher retention capacities are favored by the presence of a longer spacer between quaternary ammonium and carboxylate groups.

As it can seen from Fig. 6 the retained amount of CF constantly increases with increasing time. The equilibrium was reached very fast, 20 min for the ion exchanger with porous structure whereas for that of gel structure the equilibrium was reached in 12 h.

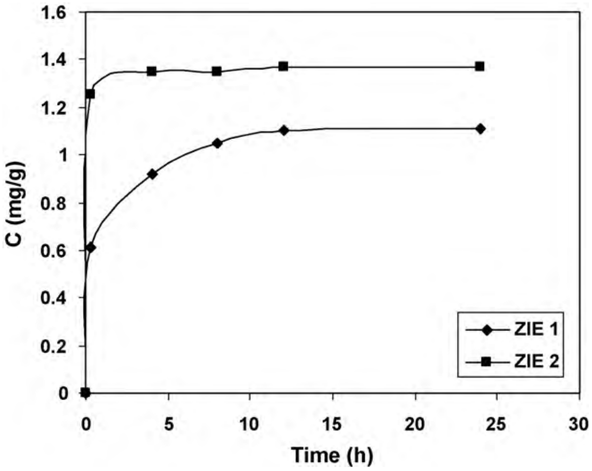


Fig. 6. Effect of the contact time on the retention capacity of CF by zwitterionic ion exchangers ZIE I at CF concentration of $7 \times 10^{-2}\,g\,L^{-1}$.

4. Conclusion

By the adequate compositions of 4-VP and DVB monomers and diluent in the polymerization process the copolymer matrices of gel and porous structure, as precursors for the zwitterionic ion exchangers have been prepared.

Betainization reactions on the 4-VP:DVB copolymers were performed by the quaternization of the copolymers with a salt of a halogen alkylene carboxylic acid namely, sodium chloroacetate followed by the removal of NaCl and nucleophilic addition of pyridine copolymers to carbon-carbon double bond of acrylic acid. The yielded compounds are zwitterionic ion exchangers with carboxybetaine moieties with one and two methylene group between oppositely charged groups namely, quaternary ammonium and carboxylate groups. This assertion was proved by the betainization degrees ≥ 90% for both structures of zwitterionic ion exchangers estimated by FT-IR spectroscopy.

Zwitterionic ion exchangers exhibited good values of the ion exchange capacities, low values of water retained capacity compared to the traditional ion exchangers as well as high selectivity to hydrogen ion. The data obtained in the retention experiments towards salts of the inorganic and organic compounds show unambiguous that these zwitterionic ion exchangers simultaneously retained the cations and anions from the aqueous solutions.

Zwitterionic ion exchangers with two methylene groups between the opposite charges and porous structure showed higher values of the C_R than the ion exchangers with carboxybetaine moieties separated by one $-CH_2-$ group and gel morphology. At the concentration of $500\,mg\,L^{-1}$ alkaline earth metals no retention capacities were obtained. In contrast to the linear polybetaines which exhibited greatly enhanced solubility and extensive chain expansion in the presence of electrolyte the crosslinked polybetaines are not capable of simultaneous interaction with both ions of added low molar mass electrolytes, i.e., KCl, NaCl, Na_2SO_4 in the work conditions of the present study.

The new structure of zwitterionic ion exchangers with carboxybetaine moieties are able to retain voluminous organic compounds, i.e., cefotaxime sodium salt from aqueous solution at high concentrations.

Interpolyelectrolyte interactions could be controlled by variation of alkyl spacer in the betaine moieties offering considerable scope for designing polyelectrolyte complexes with appropriate and predictable stability in water-salt media that could be of practical significance, in particular for the development of separation techniques.

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