

Selectivity in preparative separations of inorganic electrolytes by size-exclusion chromatography on hypercrosslinked polystyrene and microporous carbons

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Abstract

Preparative-scale separation of concentrated solutions of simplest mineral electrolytes by size-exclusion chromatography was performed on three samples of commercially available microporous hypercrosslinked polystyrene sorbents “Macronet Hypersol” and two experimental samples of activated carbons. Selectivity of separation of a pair of electrolytes was found to be determined by the largest ions in each pair. Fortunately, selectivity rises at higher concentrations of electrolytes, which was explained by exclusion of smaller species from the concentrated solution, i.e., mobile phase, into small pores of the column packing that are inaccessible to large species. The separation of concentrated mixtures revealed another remarkable advantage of the new process – self-concentrating of each of two separated components in the corresponding fractions. Self-concentration is more pronounced for the minor component that occupied less space in the initial mixture. The new method may prove productive in processing pickle bath solutions.

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1. Introduction

At present, size-exclusion chromatography (SEC) represents the most widespread method of determining molecular weight and molecular weight distribution of polymers. The method capitalizes on the difference in size of molecular species and their ability to penetrate into pores of the column packing material. Large species cannot enter smaller pores and, therefore, move with the mobile phase along the column with a higher velocity than that of smaller species which explore both large and small pores incorporating stagnant zones of the mobile phase. Though the theory that relates the size of macromolecular coils to diameters of accessible pores and the accessible portion of the total pore volume of the packing material, is far from being mature, the practical usefulness of SEC in the macromolecular research is beyond any doubt. However, SEC represents here

an analytical technique, implying injection into the column of a small portion of a diluted polymer solution, only, followed by the elution of the probe with the mobile phase. This precondition provides the independency of macromolecular coils from each other, prevents any competition between them for space available to the mobile phase in the chromatographic column. Thus far, only micro-preparative separations of macromolecular species that strongly differ in their size have been described, for instance, SEC separation of nanosponges from their clusters [1]. On a larger scale, SEC (so-called gel filtration) operates in the purification of proteins from inorganic salts, the former being excluded from a hydrogel-type packing, while small inorganic molecules enter the gel phase and reside longer in the column.

Separation of inorganic ions by analytical-scale SEC is also well documented [2–7], mainly by publications of Yoza and co-workers, on densely crosslinked hydrogels, as Sephadex G-15. Though the elution volumes of different hydrated ions were found to basically correlate with their size, the situation was often complicated by numerous side effects. Thus, interaction of nitrate or chlorate anions with the sorbent matrix or of barium

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cations with its hydroxyl groups cause retention of both these ions and their oppositely-charged partner ions, which results in the rise of the retention volumes of electrolytes over the value of the hold-up volume of the column. To the best of our knowledge, no attempts have been made to apply SEC on neutral packings for preparative separations of electrolytes.

Recently we suggested that the mechanisms of industrially important processes of “ion retardation” and “acid retardation” on amphoteric and anion-exchange resins, respectively, have much in common with SEC separations, and described a new type of preparative chromatographic process, separation of simplest mineral electrolytes by means of frontal SEC of their aqueous concentrated solutions on neutral microporous materials [8,9]. The size of hydrated mineral cations and anions is relatively small, on the level of several angströms, and so their SEC separation requires using microporous stationary phases. Very promising proved to be microporous neutral hypercrosslinked polystyrene sorbents. These materials represent the first and up to now the only microporous non-functionalized polymeric adsorbing material with the pore size comparable to diameters of hydrated electrolyte ions. Several types of neutral hypercrosslinked polystyrene sorbents are currently manufactured by Purolite International (Pontyclun, UK) on an industrial scale [10]. Another useful column packing material proved microporous activated carbons prepared by pyrolysis of beaded hypercrosslinked polystyrene sorbents [11]. Due to high rigidity of the framework of both the carbons and hypercrosslinked polystyrene, their largely hydrophobic micropores avoid collapsing and accommodate water that can be accessed by small molecules and ions.

Our previous report [9] dealt with some distinguishing features of SEC that are most important for a preparative-scale process, such as:

- species separated by an exclusion chromatography process are transported along the column by the mobile phase, but move faster than that mobile phase;
- a size-exclusion column, being equilibrated with the mixture under separation, always incorporates a liquid the concentration of which remains reduced with respect to excluded species;
- concentration of all species that appear in the corresponding fractions of the effluent in a frontal size-exclusion chromatography rises again to the level of their concentration in the initial mixture, or, in other words, frontal SEC does not cause any dilution of solutes;
- rather the opposite, separation of a concentrated two-component mixture by SEC is connected with a self-concentrating effect of the components in the corresponding fractions of the effluent, according to inherent results of an “ideal separation process”.

This communication is focused on the selectivity of the new chromatographic preparative procedure, which can be defined as the distance between the fronts of chromatographic zones of separated components, expressed, e.g., in bed volumes of the column. Selectivity, together with the extent of

self-concentrating of the components, determine the productivity of the process, thus giving an idea of the practical value of the process.

2. Experimental

2.1. Materials

Ethylene diamine tetraacetic acid (EDTA) disodium salt dihydrate, $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$, $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ and $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$ were purchased from Acros Organics (Belgium). Mercury(II) acetate was from Aldrich (UK). Other chemicals were from Reakhim (Russia). All the above compounds were used without additional purification.

Three types of hypercrosslinked polystyrene sorbents produced on an industrial scale by Purolite International (UK) were used in this study. Those are two neutral resins, MN-270 and MN-202, and a sulfonated resin MN-500. Two experimental new activated carbons, D4609 and D4610, were also received from the same company.

Following our earlier suggestions [12], Britain company Purolite Int. manufactures several types of neutral and functionalized hypercrosslinked polystyrene adsorbing resins. Among these are, first of all, neutral MN-270 and MN-202. The former represents microporous sorbent with uni-modal pore size distribution. According to information of the manufacturer [10], 50% of pores in the polymer have a diameter of 1.5 nm. Sorbent MN-202 has a biporous structure in which large transport pores of 80–100 nm in diameter penetrate microporous hypercrosslinked domains that have micropores of approximately the same diameter, 1.5 nm. It should be pointed out, however, that a reliable measurement of diameters of micropores is hardly possible, especially for rather flexible hypercrosslinked polystyrene materials that are capable of swelling even in liquid nitrogen [13]. Therefore, the above data should be used for orientation, only. As regards to pore volume of the resins, it amounts to 1.0–1.1 cm^3/g for MN-202 and 0.7–0.8 cm^3/g for MN-270. These values should apply for both dry and swollen state, since the volume of beads of the above materials does not change noticeably on wetting (at most, 5–7%).

Sulfonated resin MN-500 belongs to the same group of biporous products as MN-202 and, as a whole, has the same features of porosity. However, the introduction of noticeable amounts of the voluminous substituents (ion exchange capacity with respect to sulfonic groups is 2.2–2.8 meq/g) undoubtedly reduces accessible space in the micropores and the size of the latter.

Parameters of the porous structure of the new activated carbons based on hypercrosslinked polystyrenes, D4609 and D4610, have not been disclosed, as yet. Our experiments on pyrolysis of some hypercrosslinked polystyrenes showed [11] that the process results in about two-fold reduction of beads in size and, depending on conditions of MN-500 pyrolysis, final carbonaceous materials have pores ranging from 0.5 to 1.0 nm in diameter. Therefore, it would be logical to suppose that activated carbons examined in this work have pores of similar sizes.

2.2. Procedure

A sorbent to be tested (with beads of 0.3–1.2 mm in diameter for the polymeric sorbents and 0.3–0.8 mm for the activated carbons) was placed into a 30 ml glass column (20 cm in height). All pores in the sorbent were pre-filled with water by washing the sorbent with ethanol and then excess water. A solution of electrolytes was passed through the column from its bottom to the top (“forward” experiment). Once the column has been equilibrated with the feed solution, the electrolytes were pushed out of the column by washing the sorbent with pure water from the top to the column bottom (“reverse” experiment). In the both experiments, the liquids were transported by gravity at a flow rate of 0.5–0.7 ml/min, with fractions of the effluent of around 1.3 ml being collected by a fraction collector. By adjusting the height difference between the level of liquid in the feed reservoir and the outlet tubing of the column, it is easy to regulate the flow rate and keep it constant throughout the experiment. For a more precise monitoring of the effluent, weight of each fraction was determined, before analyzing the composition of fractions in appropriate aliquots. After the electrolytes were completely removed from the sorbent, for safety reasons, the latter was additionally washed with 250–500 ml water, and then next experiment with another pair of electrolytes was carried out.

2.3. Analysis of electrolytes

Concentration of electrolytes in each fraction of effluent was determined by titration. Concentrations of acids and bases (protons and hydroxyls) were determined by direct titration of 200 μ l aliquots with alkali or acid solutions in the presence of phenolphthaleine or methyl orange. When separating mixtures of sulfuric acid with metal sulfates, a 200 μ l aliquot of each fraction was first titrated with 0.2 N NaOH solution till methyl orange end point, to give the concentration of the excess acid. Then, an equal aliquot of the effluent was introduced into a column packed with 10–15 ml of cation exchanger Dowex 50 \times 8 in H⁺-form, followed by washing the resin with 30–40 ml of water and titrating the filtrate with NaOH, to give the sum of the free acid and that released through exchange of metal cations by protons. Thus, the concentration of FeSO₄ + CuSO₄ or Al₂(SO₄)₃ was calculated as the difference between the above two titration

results. Similarly, concentration of Na₂SO₄ in its mixture with NaOH was determined by adsorption of NaOH and conversion of Na₂SO₄ into H₂SO₄ through the ion exchange on Dowex 50 \times 8 in H⁺-form.

To determine the concentration of chloride anions, a 200 μ l aliquot of an effluent fraction was dissolved in 10 ml water, 10 ml ethanol and 4 ml of 0.5N HNO₃; two drops of Bromphenol Blue solution and seven drops of diphenylcarbazone solution were added and the probe was titrated with 0.2N Hg(OAc)₂ solution (that was provided with 3 ml of 70% HNO₃ per 1.0 l solution) until the color of the probe changes from yellow to violet.

Calcium ions in a 200 μ l probe, diluted with 20 ml water, were titrated with 0.05 M EDTA solution in the presence of murexide and 1.0 ml 5N NaOH solution, taking the change in color from crimson to lilac as end point.

3. Results and discussion

3.1. Experimental findings

Fig. 1 presents a typical chromatogram obtained by transporting a rather concentrated mixture of two electrolytes from the bottom to the top of a 30 ml column packed with a microporous material (“forward” experiment), until the column is equilibrated with the mixture, and then replacing the electrolytes from the column with pure water introduced from the top of the column downwards (“reverse” experiment). Substantial divergence of elution fronts of CaCl₂ and HCl is evident from that figure, as well as the remarkable self-concentrating within the CaCl₂ fraction and HCl fraction that can be isolated in the forward and reverse experiments, respectively.

It would be hardly possible to characterize quantitatively the results of such separation process in terms of conventional selectivity values and plate numbers. Therefore, for practical reasons, breakthrough volumes, BtV_{0.05}, were determined in the forward experiments at the 5% level of the initial concentration of each of two electrolytes under separation. From theoretical point of view, more meaningful are breakthrough volumes measured at the half of the height of the concentration waves, BtV_{0.5}. These values were estimated for both the forward and reverse experiments. In the forward experiment, the difference Δ_1 between BtV_{0.5} values of the two separated electrolytes,

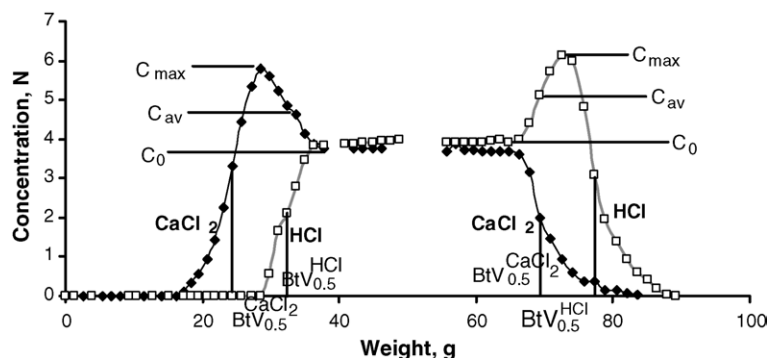


Fig. 1. SEC separation of 4N calcium chloride and 4N hydrochloric acid on D4609 carbon. Column, 30 ml in volume; flow rate, 0.6 ml/min. Feed solution (50 ml) delivered from the bottom upwards, then eluent (water) delivered from the top of the column downwards.

Table 1
Separation of electrolytes on hypercrosslinked polystyrene resins

Electrolyte	MN-270						MN-202						MN-500					
	C_0 (N)	BtV _{0.05} (ml)	BtV _{0.5} (ml)	C_{max}/C_0	Δ (BV)	P (BV)	C_0 (N)	BtV _{0.05} (ml)	BtV _{0.5} (ml)	C_{max}/C_0	Δ (BV)	P (BV)	C_0 (N)	BtV _{0.05} (ml)	BtV _{0.5} (ml)	C_{max}/C_0	Δ (BV)	P (BV)
CaCl ₂	3.6	15	22.5	1.34	0.25	0.29	3.5	18	23.4	1.14	0.20	0.22						
HCl	3.8	28	30.0	1.50	0.25	0.31	3.9	27.5	29.5	1.41	0.15	0.18						
LiCl	2.1	16.2	20.9	1.08	0.24	0.25	3.85	19.5	23.5	1.15	0.18	0.19						
HCl	2.1	25.8	28.0	1.36	0.20	0.24	4.0	26	29	1.45	0.14	0.17						
KCl	1.2	14	17.3	1.08	0.19	0.20												
HCl	4.2	21	22.9	1.08	0.17	0.18												
H ₂ SO ₄	4.0	17	22.4	1.07	0.14	0.14	4.0	20.5	24.9	1.05	0.06	0.06	4.5	18	23.2	1.00	0.05	0.05
HCl	3.9	23	26.5	1.12	0.05	0.05	3.9	23.5	26.8	1.07	0.05	0.05	3.5	19	24.6	1.06	0	
Na ₂ SO ₄	1.8	13.5	17.0	1.17	0.32	0.35												
NaOH	0.95	23	26.5	1.15														
(Fe + Cu)SO ₄	2.15	13	18.0		0.28	0.28												
H ₂ SO ₄	2.75	19	26.4															
Al ₂ (SO ₄) ₃	0.9	13	18.0		0.26	0.26												
H ₂ SO ₄	3.4	18	25.7															
CaCl ₂							1.8		23.4	1.01	0.05	0.05	4.0	19.5	23	1.00	0.05	0.05
Ca(NO ₃) ₂							1.7		24.9	1.06	0.08	0.08	4.3	19.5	24.5	1.06	0.05	0.05
NaCl							1.9		23.3	1.0	0	0						
NaOH							2.2		23.3	1.0	0	0						

Table 2
Separation of electrolytes on activated carbons

Electrolyte	Carbon D4609						Carbon D4610					
	C_0 (N)	BtV _{0.05} (ml)	BtV _{0.5} (ml)	C_{\max}/C_0	Δ (BV)	P (BV)	C_0 (N)	BtV _{0.05} (ml)	BtV _{0.5} (ml)	C_{\max}/C_0	Δ (BV)	P (BV)
CaCl ₂	3.75	17	23.6	1.56	0.28	0.36	7.3	23	27.5	1.26	0.25	0.28
HCl	4.0	30	31.0	1.54	0.24	0.30	3.1	24	35	1.84	0.13	0.18
LiCl							3.3		24.5	1.42	0.24	0.29
HCl							3.9	30	31.7	1.37	0.16	0.19
NaCl	2.8	19	25	1.24	0.33	0.37						
HCl	2.7	31	35	1.42	0.33	0.40						
H ₂ SO ₄	4.5	24	26	1	0	0	3.7	27	28	1	0	0
HCl	3.4	24	26	1	0	0	4.3	27	28	1	0.03	0.03
Na ₂ SO ₄	1.2	15.3	18.3	2.1	0.35	0.54						
NaOH	0.94	25.8	30.9	1.3								
(Fe + Cu)SO ₄	2.3	15	18.4		0.53							
H ₂ SO ₄	2.7	32	34.2	1.14	0.30	0.32						
Al ₂ (SO ₄) ₃	1.0	14	17.0		0.47							
H ₂ SO ₄	3.3	28	31.1	1.06	0.47	0.48						
CaCl ₂	4.2	16.5	21.2	1.18	0.17	0.19	3.8	22	26.3	1.13	0.12	0.13
Ca(NO ₃) ₂	4.0	23	26.4	1.04	0.15	0.15	4.5	26	30	1.03	0.07	0.07
NaCl	2.9	17.3	21	1	0.18	0.18	1.7	22.7	25.7	1	0	0
NaOH	2.7	21.6	22.5	1	0	0	2.1	23.2	25.7	1	0	0

when divided by the bed volume (30 ml), was thought to characterize the selectivity of the separation (expressed in bed volumes) with respect to the faster moving component. Selectivity Δ_2 of isolation of the slower moving component similarly results from the difference between two BtV_{0.5} values determined in the reverse experiment. These values are presented in Table 1 for a series of electrolyte mixtures examined on hypercrosslinked polystyrene-type sorbents. Note that in each pair of electrolytes, the first line of data corresponds to the faster moving electrolyte, whereas second line of data characterizes the slower moving component. Table 2 presents the corresponding data for the two activated carbons examined.

One can note that the electrolyte separation selectivity Δ in the frontal SEC process can amount to astonishingly high values, up to 0.5 bed volumes of the column. Noteworthy is also the fact that the Δ_1 and Δ_2 values for the two separated components do not need to be equal.

Second important quantitative parameter of the separation process is the degree of self-concentrating of the isolated electrolytes, expressed as the ratio of the maximum concentration, C_{\max} , of the corresponding isolated electrolyte to its initial concentration, C_0 , in the feed mixture. The self-concentrating effect definitely enhances the practical value of the new process, its total productivity. For the practice, it is advisable to estimate the concentration C_{av} , graphically averaged over the total span Δ of fractions that contain isolated components, and the averaged self-concentrating coefficients C_{av}/C_0 for each of the two electrolytes. A product P of the Δ values with the corresponding averaged self-concentrating coefficients will then characterize the total productivity of the separation process; it is expressed in bed volumes (BV) of the initial mixture from which the cor-

responding electrolyte can be (theoretically) isolated:

$$P = \frac{\Delta C_{\text{av}}}{C_0}$$

3.2. Size of ions and selectivity of their separation

According to [14], the interstitial volume of a column that is packed with a beaded material of broad bead size distribution amounts to about 40% of the column volume. For a 30 ml column used in our experiments, the interstitial volume thus amounts to circa 12 ml. In addition to this volume, the mobile phase (water) also occupies the porous volume within the sorbent, which can be evaluated from the true density and porosity of the material. We estimated directly the total volume of the mobile phase in the columns filled with the material MN-270 and MN-202 as 21.5 and 24.6 ml, respectively, by weighting out dry polymer, dry column and the column filled with the polymer and water.

Theoretically, elution volumes of components separated in accordance with the SEC mechanism should vary between 12 ml for a totally excluded component and 21.5 and 24.5 ml for MN-270 and MN-202 columns, respectively, for species of the size of a water molecule. The difference between elution volumes of the above extreme solutes should not be expected to exceed the total porous volume of the packing material, i.e., 9.5–12.5 ml or roughly one third of the column bed volume (BV). However, the practically attainable selectivity (Δ) of the process may exceed this theoretical value several-fold, when working with highly concentrated electrolyte solutions.

As follows from Fig. 1 and Tables 1 and 2, in frontal chromatography experiments, fronts of CaCl₂, LiCl, NaCl and KCl

move significantly faster through the SEC column than the front of HCl. In [9], we stated “Since the salts and the acid in the above systems have the same chloride anion, the divergence of the salt and acid fronts is due to different behaviors of the proton and the metal cations in the (hypercrosslinked) sorbent phase.” This logical statement, however, does not generally imply that the distance between the two fronts, i.e., selectivity of separation, is determined by the difference in sizes of the above metal cations, on one side, and that of hydrated proton, on the other.

First of all, the effective size of protons (hydroxonium ions) in the considered chromatographic system can be set close to zero. As explained in [9], protons and hydroxyl anions do not need to migrate through the column, at all, since a rapid shift of electrons along “a hydrogen-bonded water wire”, the chain of hydrogen bonds between water molecules in an aqueous media, can immediately generate a positive or negative charge, i.e., a hydroxonium or hydroxyl ion, respectively, in any position of that aqueous phase where a charge is required. In fact, the electron-proton-coupled transfer of a charge in an aqueous phase proceeds by electrons hopping along the “wire” with the protons in the chain of hydrogen bonds hopping in the opposite direction. Therefore, the migration velocity of the HCl front is entirely determined by the movement of chloride anions, rather than that of protons. Due to the local electroneutrality principle, protons emerge in close vicinity of moving chloride anions, probably, without retarding noticeably the movement of the latter. Similarly, the migration velocity of a base MOH through a neutral sorbent bed must be entirely determined by the rate of migration of the M^+ cation, with the hydroxyl anion emerging close to the moving cation.

As to the velocity of the front of a metal chloride, it must be largely determined by the rate of movement of the largest ion of the salt, which is stronger excluded from the porous space of the packing material and, therefore, has to migrate faster than the smaller counter-ion. Of the ions under consideration, hydrated radius [15] of cations Ca^{2+} , Li^+ and Na^+ decreases in the given order (4.12, 3.82 and 3.58 Å, respectively), all of them being larger than the Cl^- anion (3.32 Å). Of course, chlorine anions are bound to migrate right after their larger partner cations, probably slowing down the resulting velocity of the pair to a certain degree.

From this consideration it logically follows that the total selectivity of separation of two electrolytes, MCl and HCl, is mainly caused and determined by the difference in sizes of the cation M^+ and anion Cl^- , the largest ions of the two electrolytes under separation, not those two ions (M^+ and H^+) that make the electrolytes differing from each other. This rather non-trivial for chromatography expectation finds a strong support in the results of separation of two pairs of electrolytes, NaCl/HCl and NaCl/NaOH on carbon D4609. In the first pair, the rate-determining species are Na^+ and Cl^- with ionic radii 3.58 and 3.32 Å, respectively [15]. The difference in their size is not too large, but, obviously sufficient for a successful separation. As illustrated in Fig. 2, fronts of NaCl and HCl diverge by one third of the total bed volume ($\Delta = 0.33$), both in the forward and reverse experiments. In the pair NaCl/NaOH, the largest ion is Na^+ for the both electrolytes, and only a poor separation

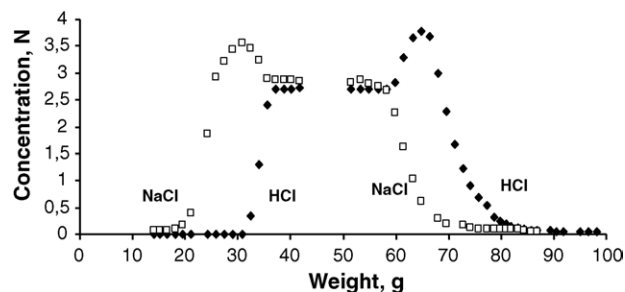


Fig. 2. SEC separation of 2.5N sodium chloride and 2.7N hydrochloric acid on D4609 carbon. Experimental conditions, similar to those in Fig. 1.

is observed in the forward experiment ($\Delta = 0.18$) with no separation at the tail of the chromatographic zones (Fig. 3). This result could not be explained, if we would try to compare sizes of cations Na^+ and H^+ in the first pair and anions Cl^- and OH^- in the second pair, though these ions distinguish the electrolytes in each pair and represent the target and the actual result of the separations.

In contrast to the remarkable separation of the above NaCl/HCl pair, Na_3PO_4 is not separated from H_3PO_4 on the same carbonaceous material. Certainly, hydrogen phosphates Na_2HPO_4 and NaH_2PO_4 dominate in the feed solution, and these large phosphate anions determine the migration velocity of the both electrolytes. Smaller cations of Na^+ and H^+ in this system are bound to follow the leading phosphate anions without being separated at the end.

Tables 1 and 2 demonstrate that alkali cations govern the separation, if combined with small anions, like Cl^- , only. When judged by the values of Δ , on all sorbents tested, the selectivity of separation of HCl from metal chlorides logically increases in the series $K^+ < Na^+ < Li^+ < Ca^{2+}$, along with the increase in the radius of the above hydrated cations.

In combination with the larger anion SO_4^{2-} ($r = 3.79$ Å), only polyvalent cations have a chance to significantly contribute to the separation. Indeed, Cu(II), Fe(II) and Al(III) sulfates readily separate from sulfuric acid. Hydrated radii of these cations are estimated to amount to 4.19, 4.28 and 4.75 Å, respectively [15].

Where hydrated cations exceed in size their anions, the breakthrough volumes of the salt correlates with the size of the cation. Largest cations appear in the effluent very early. Measured at the

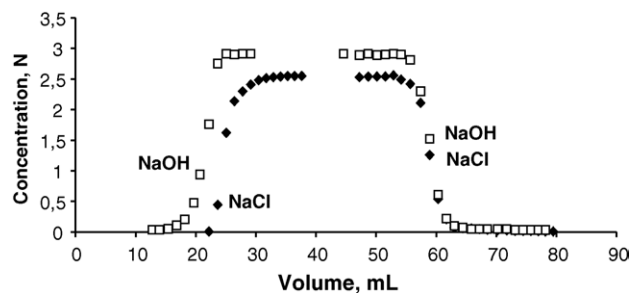


Fig. 3. SEC separation of 3.9N sodium chloride and 2.5N sodium hydroxide on D4609 carbon. Experimental conditions, similar to those in Fig. 1.

level of 5% of the zone height ($BtV_{0.05}$, ml), the sequence of elution of salts on sorbents examined is as follows:

MN-202: $Ca^{2+}(18) < Li^+(19.5)$;
 MN-270: $Al^{3+}(13) \approx Fe^{2+}(13) < Ca^{2+}(15) < Li^+(16)$;
 Carbon D4609: $Al^{3+}(14) < Fe^{2+}(15) < Ca^{2+}(17) < Na^+(19)$.

3.3. Influence of concentration and “salting-out” effects

Whereas ion chromatography and capillary electrophoresis, as efficient analytical techniques, develop toward increasing the sensitivity and resolution (efficiency), SEC of electrolytes may have an opposite application niche, i.e., preparative and industrial processing of concentrated solutions. For this reason, all our experiments were carried out on concentrated electrolyte mixtures, which is quite unusual for chromatography. From theoretical viewpoint, the separation capacity of a size-exclusion column with respect to the volume of the sample has an upper limit that is determined by the total porous volume of the packing material. In the best possible case, the elution front of a smallest species can fall behind the front of a totally excluded component by the total volume of pores. To the best of our knowledge, the role of the concentration of species in SEC has not been previously examined. Fortunately, in our experiments, increasing the concentration of electrolytes in the sample was found to enhance not only the overall productivity of the process, which is rather trivial, but also the selectivity of separation.

Thus, raising the concentration of LiCl up to 12N in its mixture with 0.06N HCl was found to widen the gap between the breakthrough fronts of LiCl and HCl up to more than five bed volumes. In [16], we suggested, that explanation of this unexpected phenomenon requires consideration of concentration gradients in the mobile phase. LiCl is excluded from a certain part of the porous volume and exists as the concentrated (12N) solution in the interstitial space and within larger pores. Meanwhile, the mobile phase within smaller pores can be expected to become 0.06N in HCl, only. Because of the extreme gradients in the concentration of common Cl^- anions, the latter are forced into those diluted domains of the mobile phase. Chloride ions can easily accumulate there in the form of HCl (not LiCl). Since there is no movement of the mobile phase through the porous space, HCl remains retarded in the stagnant zones of small pores, until the concentration of common Cl^- anions there becomes comparable with that of the feed solution. This situation can be compared with known “salting-out” effects or with some kind of “retention” of HCl by an “immobilized liquid phase”. We can also speak of steric exclusion of larger species from the stagnant portion of the mobile phase in the micropores, combined with the gradient-driven exclusion of smaller species from the moving part of the mobile phase into the micropores. A porous material thus brings about differentiation in space of the two electrolytes confined in the porous space and, in addition, levels out concentration differences of these electrolytes with respect to the common ion.

On eluting the above electrolytes from the column with water, HCl emerges in the effluent immediately after the LiCl zone in

the form of a sharp zone with a concentration of up to 0.9N, i.e., with a 15-fold self-concentrating effect.

We believe similar strong concentration gradients to operate in many (not all) examined systems. Otherwise, it would be difficult to explain why two elution fronts in a mixture like NaCl/HCl diverge by as much as one-third of the column volume, in spite of the rather small difference between the sizes of the situation-determining ions of Na^+ and Cl^- . Here, “retention” of HCl in the “immobilized liquid phase” most probably contributes to its separation from NaCl by the size-exclusion effect. On the contrary, NaOH cannot be excluded into and “retained” in a stagnant compartment of the mobile phase, since no extra space is available to NaOH as compared to NaCl, both of which being restricted to the pores accessible for the same large Na^+ cations.

3.4. Self-concentrating effects and productivity of separation

The practical value of a preparative chromatographic procedure is usually evaluated on the maximum volume of the sample that can still be tolerated by the column and the concentration of that sample. The two parameters usually counteract each other. From this viewpoint, SEC of electrolytes appears superior to all other chromatographic techniques in that the volume loading of a column in many cases increases with the rise in the concentration of the feed. This phenomenon results from the unique advantage of the new technique, that becomes evident on working with concentrated feed solutions, namely, that the separated components appear in the effluent with remarkably enhanced concentrations. Tables 1 and 2 illustrate this self-concentrating effect with the ratio C_{max}/C_0 between the maximum concentration of a component zone to the concentration of the component in the initial feed solution. Depending on the total concentration of the feed and the proportion of the components, the value of C_{max}/C_0 varies in a broad range, amounting to 15 in the above-discussed case of a dilute solution of HCl in a concentrated LiCl solution.

The self-concentrating phenomenon was explained in our previous report [9] in terms of an “ideal separation process”, defined as a process that does not introduce any additional matter (e.g., additional eluent) into separated fractions of the initial sample. In such a process, self-concentration is the unavoidable

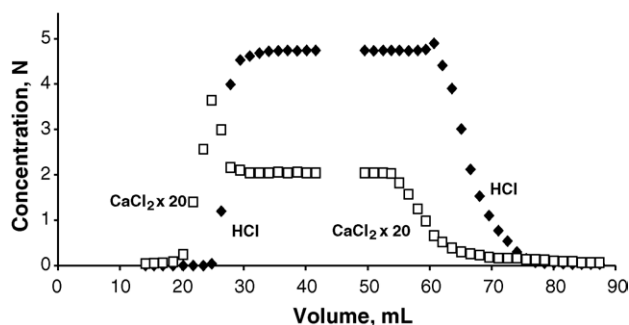


Fig. 4. SEC separation of 0.1N calcium chloride and 4.7N hydrochloric acid on D4609 carbon. Experimental conditions, similar to those in Fig. 1. Note: concentration scales for HCl and $CaCl_2$ differ by a factor of 2.0

result of removing of one (or several) component(s) from the initial mixture. It was also reasoned that the self-concentrating effect must be more pronounced for the minor components of the mixture: the more matter (i.e., major component) is withdrawn from the mixture, the stronger rises the concentration of the remaining minor components. Minor component in this context is the one that occupies less space in the initial mixture. For an electrolyte it means that its concentration is smaller and/or its hydrated radius is smaller. Indeed, data in Tables 1 and 2 show that, at comparable concentrations of two components, the last eluted one is stronger concentrated, because its hydrated ions are smaller and occupy less space. An extreme value of $C_{\max}/C_0 = 15$ for the above example with 12N LiCl and 0.06N HCl is the result of combined action of three factors: low concentration of HCl, its smaller effective molar volume, and the above-discussed “salting-out” effect. An opposite result (Fig. 4) was achieved with a solution 5.0N in HCl and 0.1N in CaCl₂, separated on carbon D4609. Here, the concentration of CaCl₂ in the first eluting zone peaks up to 1.8 of the initial value, whereas concentration of the last eluting major component, HCl, rises insignificantly. In this system, the “salting-out” effect of the minor component into a small stagnant zone cannot operate, since CaCl₂ does not fit into the small pores. Besides, the factor of molar volume difference of the two electrolytes acts counterproductively. Hence, the smaller extent, 1.8, of the self-concentration of the minor component, which is entirely due in this system to the fact of separation, i.e., removing HCl from the minor component, CaCl₂.

The “ideal separation process” naturally divides the volume of the sample that was introduced into the column in two smaller parts, which raises the loadability of the column. If, in a favorable case, this factor combines with the “salting-out” effect of the minor component, the total productivity of the column increases substantially. In the above considered extreme case of removing trace HCl from the concentrated LiCl solution, more than five bed volumes of the feed can be processed before the two elution zones start overlapping. The minor component, HCl, that meanwhile concentrates in the column, elutes with water in the form of a sharp peak. We feel therefore, that a reasonable measure of the column productivity P in the SEC process considered could be the product of the zone width with the averaged self-concentrating coefficient. The resulting P -values are summarized in Tables 1 and 2, showing that the column productivity easily rises to 0.3–0.5 bed volumes for comparable concentrations of two electrolytes.

4. Conclusion

The novel process of size-exclusion chromatography of mineral electrolytes on non-functionalized microporous hypercrosslinked polystyrene and activated carbons on their basis

appears to be of significant interest from both practical and theoretical points of view. Selectivity of separation was shown to be determined by the largest ions in each pair under separation. Distinct to other types of chromatography, the separation selectivity in SEC of electrolytes increases parallel with the increase in the concentration of the initial mixture. In addition to this favorable dependence, the practical value of the technique is further enhanced by the unique self-concentrating effect of the both separated components. In accordance with the concept of “ideal separation process”, the self-concentrating of the two components automatically results from the vary fact of their separation.

High selectivity, combined with the self-concentrating effect of resolved components, render the SEC approach as one of great practical importance. Besides, the process requires no auxiliary reagents and generates no mineralized waste flows. Thus, processing of acidic pickle bath solutions, in order to isolate Cu, Al, Ni, etc. and save excess sulfuric acid, can prove economically feasible. Separation of more complex mixtures of electrolytes may also present practical interest.

Further studies are under way, aimed at revealing the role of the porous structure of column packing, extent of hydration of ions under separation, contribution of possible additional interactions of ions with the packing material, effects of temperature, flow rate, and many other details of the new technique. Still, at the present stage the nature of basic processes is believed to be largely understood. This stage already reduces empirical work and allows making certain predictions to be then checked in a purposefully planned experiment.

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