

# Competition between ions in size exclusion chromatography of electrolytes on neutral microporous materials

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DOI: 10.1070/MC2005v015n05ABEH002134

Competition between hydrated ions for accessible porous space within particles of non-functionalised microporous sorbents (hypercrosslinked polystyrene or microporous carbonaceous materials) in the size exclusion chromatography of concentrated solutions of mineral electrolytes results in the enhancing of both the selectivity of separation and the self-concentrating effect of resolved components.

Recently,<sup>1</sup> a process has been suggested for the preparative separation of mineral salts, acids and bases – size exclusion chromatography (SEC) of electrolytes on neutral microporous adsorbing materials. The new process fundamentally differs from conventional ion exchange chromatography (IEC) that represents a traditional approach to separating electrolytes in that the SEC column packing material contains no functional groups capable of electrostatic interactions with the ions under separation. Instead, the SEC process separates hydrated ions in accordance with their size. The first immediate advantage of SEC is that the elution process of electrolytes from the column does not require any displacing reagent, any acid or base. Pure water takes the ions through the column, so that the latter does not need any regeneration after the water wash. For this reason, no waste streams are generated, which, in the case of regeneration of ion exchange columns, represent highly mineralised solutions, which are expensive to dispose. The second important advantage of SEC of electrolytes is that the process is non-stoichiometric. For this reason, the fundamental concept on exchange capacity or adsorption capacity of the column is no more applicable, and the concentration of the sample solution can be selected arbitrarily. Of course, the solubility of sample components sets a threshold for concentrations, and the volume of micropores in the column packing limits the volume of the sample that can be separated in one chromatography cycle. Still, the possibility of processing relatively large volumes of extremely concentrated electrolyte solutions enhances the industrial importance of the new process and favourably distinguishes it from all known chromatographic and ion-exchange separation technologies.

To the best of our knowledge, the SEC approach to the preparative separation of mineral low-molecular-weight electrolytes has not been examined, probably, because no suitable rigid microporous neutral packing materials were available. Hypercrosslinked polystyrene, the only known class of hydrophobic microporous polymeric materials, was first introduced by Davankov and Tsyurupa,<sup>2,3</sup> in the early 70s, but they became commercially available<sup>4</sup> only in the 90s. Industrially manufactured adsorbing materials of the hypercrosslinked polystyrene nature are known as Hypersol-Macronet (Purolite, Pontyclun, UK), Lewatit VP OC 1163 and Lewatit S 7768 (Bayer Chemicals, Germany). In our experiments, we used Hypersol-Macronet, which has a sufficient amount of micropores with the maximum of pore size distribution in the range between 2 and 3 nm. Another useful microporous non-functionalised material proved to be activated carbon D4609 that was prepared from a hypercrosslinked polystyrene sample by pyrolysis.

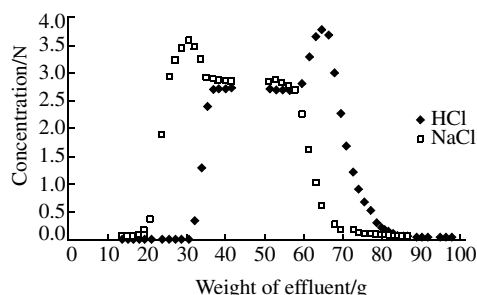
When applying concentrated mixed solutions of electrolytes (mineral acids, salts and bases) on columns 20 cm in height and 30 ml in volume, we observed<sup>1</sup> efficient separations of salts from corresponding acids, *e.g.*, LiCl, KCl or CaCl<sub>2</sub> from HCl; Na<sub>2</sub>SO<sub>4</sub>, FeSO<sub>4</sub> or Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> from H<sub>2</sub>SO<sub>4</sub>; salts from corresponding bases, *e.g.*, Na<sub>2</sub>SO<sub>4</sub> or NaCl from NaOH; several salts from each other, *e.g.* CaCl<sub>2</sub> from Ca(NO<sub>3</sub>)<sub>2</sub>. In each case, salts eluted from the column ahead of corresponding acids and bases. In terms of the differentiation of hydrated ions according to their size, these facts have been explained<sup>1</sup> by the assumption that, in

dynamic systems, the effective radii of protons and hydroxyl ions in the aqueous phase are much smaller than those of all other cations and anions. This is because protons and hydroxyl ions do not need to move through the SEC sorbent bed at all. Instead, *via* a very quick shift of electrons along a chain of hydrogen bonds between water molecules, protons and hydroxyls can be immediately generated in any position of space where a positive or negative charge is required, in order to maintain local electroneutrality. As to all other hydrated ions, they tend to move along the SEC column the faster, the larger their size, *i.e.*, the more efficient they are excluded from the sorbent bed.

Above principles apply to both diluted and concentrated solutions of electrolytes. The latter, being most interesting for industrial separations, deserve a more detailed attention. When operating with highly concentrated feed solutions, we revealed several phenomena that have not been observed in chromatographic systems before. They are briefly described in this communication and explained in terms of competition between the ions under separation for space that is available for the mobile phase within the sorbent beads and in the chromatographic column as a whole.

A typical chromatographic experiment consists of two steps (Figure 1). Through a small chromatographic column that was filled with a non-functionalised microporous sorbent and washed with water, a concentrated mixed solution of two electrolytes was introduced at a flow rate of about 0.75 ml min<sup>-1</sup>. The effluent was collected in fractions of about 1.5 ml, and the concentration of each electrolyte in the fractions was determined by conventional volumetric analysis of Cl<sup>-</sup> anions and H<sup>+</sup> cations. In this first step, the breakthrough curves of each component of the initial mixture were determined. In the second step, the column was washed with water and the concentration of electrolytes in the effluent was also determined. As seen in Figure 1, the two components move along the column at different velocities, so that at the first step a pure fraction of the faster moving component can be obtained, while the second step provides another target fraction of the second pure component that moves at a slower rate. All intermediate fractions contain an unresolved mixture identical to the initial feed.

It has been shown<sup>1</sup> that the non-functionalised microporous column packing materials do not display any significant affinity to the electrolytes examined. Their separation is basically due to the difference in the size of the hydrated ions under separation.



**Figure 1** Separation of a mixture 2.85 N in NaCl and 2.7 N in HCl on a column with a carbonaceous beaded material (0.3–0.8 mm).

Large ions have little chance to enter the micropores of the sorbent, they mostly reside in the interstitial volume, where the moving mobile phase takes them to the outlet of the column. Small ions enter the interior of the beads and reside for a while in the stagnant zones of the eluent, thus arriving at the outlet at a later point. Figure 1 gives an idea that the distance between the fronts of the two components can amount up to half a column volume, what speaks of an extremely high productivity of the new separation process.



The first most intriguing result of the separation of concentrated mixtures is that the pure components in the two target fractions, which now are free of the second partner, appear at concentrations significantly outperforming their concentrations in the initial mixture. This phenomenon unusual for chromatography can be understood in terms of an ideal separation process. We define it as a process that does not introduce additional matter into the separated fractions of the initial mixture. In such an ideal process, the separation of components automatically increases their concentrations in the resolved fractions. Indeed, the separation process removes one (or several) components from the mixture, thus reducing the volume of the latter and increasing the concentration of the remaining component in that fraction. From this new concept, it follows that the rise in the concentration of a minor component must be more pronounced than that of the major component, since the more matter is removed from the mixture, the stronger the concentration of the remaining component is affected. The concept on an ideal separation process also logically explains why the self-concentrating effect has not been noticed in numerous conventional analytical-scale SEC separations, where the concentrations of initial mixtures were traditionally low.

Even more surprising is the fact that, with the concentration of the feed mixture rising, the distance between the fronts of the two components under separation noticeably increases. This corresponds to a rise in the separation selectivity, which further enhances the productivity of the new process. An analogous phenomenon was observed by Nelson and Kraus<sup>5</sup> in the separation of concentrated solutions of LiCl from HCl on an anion exchange resin Dowex-1 $\times$ 10. The increasing retention of HCl at the concentration of LiCl rising, the authors explained by a drop of the activity coefficient of HCl in the resin phase. We believe the phenomenon to be of a more general nature and result from competition between ions for water in a concentrated solution and the location space rather than from the drop of activity coefficient of one component of the system. It is generally accepted in SEC that large species can locate in the interstitial volume of the column and in the large pores, only. Small species can additionally penetrate smaller pores. Therefore, the distance between the elution fronts of the two com-

ponents in frontal chromatography (or the distance between elution peaks in an elution process) equals the total volume of fine pores that are accessible to small species but inaccessible to large ones. This fully corresponds to experimental findings with dilute mixtures, where small and large species behave independently. With the concentration of the system rising, the ions start to experience deficiency of water that is needed for their hydration. Small species start to recognise a great difference between the total concentration of electrolytes in the fine pores and that in the other two mobile phase compartments, *i.e.*, large pores and interstitial volume. In the fine pores, the smaller species do not compete for water with the larger species. In other words, though the whole volume of the mobile phase in the column theoretically remains accessible for smaller species, they will tend to concentrate in small pores in order to minimise concentration gradients within the mobile phase. Small species will preferably reside in the fine pores until the highly concentrated solution of larger species passes by. In this case, we can also speak of the larger species ‘salting out’ the smaller ones into the mobile phase compartment that is inaccessible for large species. Thus, by applying a feed mixture that is 12 molar in LiCl and 0.06 molar in HCl, the latter was observed to reside in the column (filled with hypercrosslinked polystyrene) as long as five bed volumes of the feed were pumped through. As water was then introduced into the column, HCl was immediately eluted, at a concentration of 0.9 mol dm<sup>-3</sup>. In other words, the self-concentrating effect for HCl amounted to a factor of 15! Naturally, self-concentrating of the LiCl solution did not occur since its initial HCl content was very low anyway.

The productivity of the new size exclusion chromatography process on neutral microporous sorbents thus rises significantly in parallel with the concentration of electrolytes in the feed mixture. This effect is due to the unprecedented simultaneous increase in the following three parameters of the process (i) mass-loading on the column, (ii) selectivity of separation and (iii) self-concentrating effect of separated components.

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Received: 1st February 2005; Com. 05/2457