

Chapter 2

Ion Size Exclusion Chromatography on Hypercrosslinked Polystyrene Sorbents as a Green Technology of Separating Mineral Electrolytes

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Abstract The review considers a new preparative method of separating concentrated solutions of mineral electrolytes into individual components by size exclusion chromatography on neutral nanoporous hypercrosslinked polystyrene sorbents NanoNets (Purolite International Ltd., UK and USA). Basic principles of the method as well as factors determining the selectivity of separations are discussed. Unprecedented effect of a spontaneous increase in the concentration of separated components is explained on the basis of the concept of ideal separation process. The unprompted partial resolution of inorganic salts into parent acids and bases is a logical consequence of the size exclusion mechanism of ion separation; at the same time, this resolution proves the correctness of our understanding of the separation mechanism. The review discusses briefly previous works in this field and true reasons for well-known “acid retardation” process, the process of separating mineral acids from their salts on anion exchange resins under conditions excluding ion exchange.

2.1 Introduction

Many enterprises face the challenge of utilizing waste aqueous concentrated mixed solutions of mineral acids, bases and salts. Such kind of by-products is formed on industrial manufacturing inorganic compounds, like mineral fertilizers or soda. Galvanic wastes of mechanical engineering and electronic industries as well as waste pickling solutions produced by metal treatment and hydrometallurgy also have to be processed. As a rule, these products represent acidic or basic solutions of various salts of iron, zinc, tin, nickel, cadmium, bismuth, titanium, copper, etc. The extraction of valuable metals from these rather concentrated acidic or basic solutions by means of conventional ion exchange is not promising for many reasons, including,

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but not limited to, an unsatisfactory selectivity of ion exchange in a number of cases, the shrinkage of resin beads in concentrated solutions, which diminishes the efficiency of column operation and the resin lifespan. Besides, a rapid consumption of resin exchange capacity on processing concentrated electrolyte solutions and, correspondingly, a frequently repeated regeneration of ion exchangers substantially increase the process cost. Moreover, every regeneration cycle produces mineralized waste solutions requiring additional care.

Several attempts have been made to resolve the above problem. A real success in the processing and/or separation of electrolytes by the “ion retardation” process was achieved with amphoteric “snake-cage polyelectrolytes” suggested by Hatch et al. (1957) in 1957 and defined as “cross-linked polymer system containing physically trapped linear polymer”. Soon Dow Chemical Co. commercialized these materials under the trade name “Retardion” Dow Chemical Co. Retardion-550WQ2 (water content 41.6%), a typical snake-cage amphoteric polyelectrolyte, was made by polymerizing vinylbenzyl-trimethyl ammonium chloride inside a sulfonated polystyrene-type cation exchanger Dowex-50 W \times 2 and had both strong basic and strong acidic functional groups. On a 100 mL column packed with this resin, a 20 mL sample (2.0 N in NH_4NO_3 and 1.6 N in HNO_3) was almost completely separated into its constituents (Hatch and Dillon 1963). Similarly, 1.98 N FeCl_2 was partially separated from 3.15 N HCl. In both cases, the acids resided in the column longer than the salts.

In 1958 in a theoretical study on the activity coefficients of electrolytes in the anion exchange resin phase (Dowex 1 \times 10), Nelson and Kraus (1958) arrived at the conclusion that the separation of HCl from corresponding salts occurs, probably, due to a low activity of HCl in the phase of the anion exchanger. They reported that the breakthrough curve of 0.1 N HCl shifts to 1.5 bed volumes if the acid was dissolved in 5 N LiCl, while the acid retention rises to 8 bed volumes when the salt concentration increases to 16 N.

Five years later Hatch and Dillon (1963) described again the separation of excess acids from their salts on standard exchangers under conditions that exclude ion exchange. This separation contradicted the conception of “ionic exclusion”, according to which all strong electrolytes are excluded from ion exchange resin phase due to Donnan’s effect (Helfferich 1962; Wheaton and Bauman 1953). The strong basic anion exchange polystyrene-type resin Dowex-1 \times 8 was found to function especially well, and the authors introduced a new term “acid retardation” defining the process in which an acid moves along the column slower than its salt. The acid retardation process can be performed at high flow rates and elevated temperatures. The process was optimized and since 1976 widely exploited by Eco-Tec Canada (Brown et al. 1997; Brown and Fletcher 1988), as well as by others (Götzelmann et al. 1987) on the industrial scale.

Concerning the mechanism of acid retardation, Hatch and Dillon (1963) note that various ideas or their combinations may be offered to explain the retention of strong acids (e.g. HCl) from their salt solutions on anion exchange resins (in the acidic, e.g. chloride form):

1. Electrolyte interactions, including “salting effects”, the HCl being salted-out into the resin phase.
2. Interaction of protons of the strong acid with benzene rings of the resin matrix.

3. Association of strong acids to form ion pairs and non-ionized molecules in the resin phase, due to the low dielectric constant of that phase.
4. Possibly an entropy-increasing or energy-lowering effect of excess protons on the microstructure of the water inside the resin matrix.

However, having examined many experimental data, Hatch and Dillon (1963) concluded that “none of the ideas are proved by the data currently available”.

During the 50 years that passed since the publication of these classical studies, several research groups examined acid retardation processes on ion exchangers, but new ideas have not been suggested for the explanation of the non-trivial phenomenon of electrolytes discrimination. Interestingly, a more or less adequate mathematical description of experimental data is possible both in terms of self-association of acid molecules in the homogeneous resin phase and/or association of acid molecules with the functional groups of the resin (Soldatov et al. 2004) and in frames of a heterogeneous, two-phase model of the resin bead (Ferapontov et al. 1999). However, the first approach is based on the above ideas that have been formulated, considered and still rejected by the pioneers of the method. And suggesting heterogeneous structure for gel-type anion exchangers, supposedly composed of a swollen polymer and a separate phase of “free” water, lacks any experimental corroboration. In fact, several mathematical models may well fit experimental data into equations, but this fact does not prove the reality of the conceptions they are based on.

When analyzing the publications concerning acid retardation process, we arrived at the conclusion that the effective discrimination of an acid and its salt is conditioned on steric inaccessibility of narrow internal spaces in the bead of anion exchange resin to large hydrated metal cations, rather than any attractive interactions of the acid with styrene-divinylbenzene matrix or functional groups of standard anion exchangers. In other words, we believe that the separation of mineral electrolytes proceeds via mechanism of size exclusion chromatography.

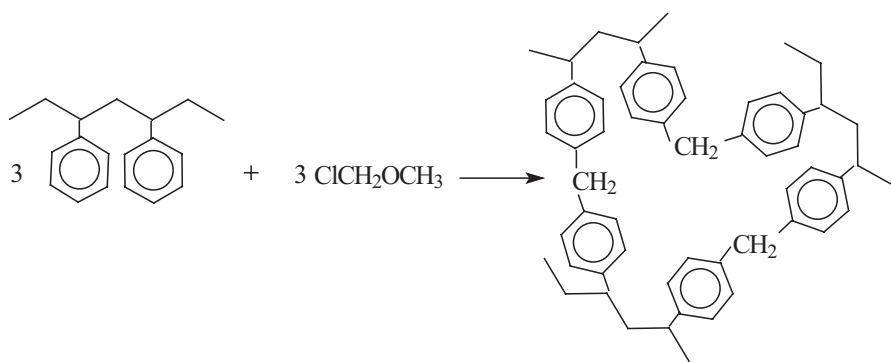
Size exclusion chromatography separates particles, macromolecules and low molecular weight compounds in accordance with their size and ability to migrate into fine pores of column packing. Large particles that can diffuse only into the widest pores mostly reside in the interstitial space and hence are rapidly transported along the column by the flux of mobile phase. Smaller particles penetrate into stagnant zones of both large and small pores and reach later the column outlet. However, to exploit this method for separation of the simplest hydrated mineral ions (diameters of hydrated ions being around 6–10 Å), it is necessary to take advantage of a sorbent having small pores. The progress we made in separation of electrolytes was conditioned upon the choice of hypercrosslinked polystyrene as the column stationary phase.

2.2 Nanoporous Hypercrosslinked Polystyrene Sorbents

Davankov and Tsyurupa (Davankov et al. 1969; Davankov and Tsyurupa 1990) were the first to introduce the hypercrosslinked polystyrene sorbents as far back as 1969. 25 years later Purolite International Ltd. (UK, USA) started to produce

these materials as Hypersol Macronet™ on an industrial scale. Nowadays, hypercrosslinked polystyrene sorbents are widely used in industrial adsorption processes (Tsyurupa 1995; Davankov et al. 2002; Davankov and Tsyurupa 2011) as well as in analytical chemistry. Thus, in environmental analysis they are used as the best sorbents for solid phase extraction (Purosep, Isolute, LiChrolut EN), because the hypercrosslinked sorbents efficiently take up and concentrate the trace amounts of both non-polar and polar organic compounds from aqueous solutions and air. It has also been reported (Proskurina et al. 2007) that distinct from the situation with other SPE-materials, many aromatic and polar organic substances can be concentrated on hypercrosslinked polystyrene even from aliphatic hydrocarbon solutions. Microbeaded hypercrosslinked polystyrene sorbents proved to be very promising column packing materials for high performance liquid chromatography. Since hypercrosslinked polystyrene is compatible with any kinds of organic and aqueous mobile phases, it is possible to conduct experiments in different HPLC modes using the same column (Sychoy et al. 2004, 2009). It is interesting to note that non-functionalized hypercrosslinked polystyrenes exhibit affinity to some heavy metal ions such as mercury, bismuth, lead or silver which form labile complexes with the π -electron systems of the aromatic polymer (Tsyurupa et al. 2003).

The above theoretically interesting and practically useful properties of hypercrosslinked polystyrene are determined by the high accessibility of aromatic network fragments to small molecules. Indeed, hypercrosslinked polystyrene is obtained by intensive crosslinking polystyrene chains in the presence of a solvent that solvates well the polymer chains and prevents them from microphase separation (Davankov and Tsyurupa 2011). Reaction of a bifunctional crosslinking agent with polystyrene phenyl rings results in obtaining rigid open-network construction composed of mutually condensed and conformationally rigid meshes:



The material thus obtained represents a transparent single-phase polymer with a reduced density of about $0.5\text{--}0.7\text{ g/cm}^3$ and high apparent specific surface area of $1000\text{--}2000\text{ m}^2/\text{g}$. The unusually large free volume of hypercrosslinked network, up to $0.6\text{ cm}^3/\text{g}$, as a matter of fact, is a true porosity of a new type, because the “pores” here correspond to small spaces confined by network meshes or, what is the same, to the openings between neighbor polystyrene chains, rather than to canals between

dense polymeric walls. The maximum of the narrow “pore” size distribution corresponds to 1.5–3 nm depending on the conditions of network synthesis. The internal free space in the hypercrosslinked network is readily accessible to molecules of gases as well as liquids, irrespective of whether the latter strongly solvate the hypercrosslinked polystyrene network (typical solvents for linear polystyrene as toluene, dichloromethane) or display little affinity to polystyrene (precipitate polystyrene from its solutions, as hexane, methanol). Even water can occupy the network internal volume because water does not cause any shrinkage of the dry nanoporous material. Thus, the internal space in hypercrosslinked polystyrene network becomes easily accessible to molecules dissolved in water or organic liquids.

2.3 Brief Description of Chromatographic Experiments

The majority of experiments were performed using nanoporous hypercrosslinked polystyrene sorbents NanoNet (NN) manufactured by Purolite International. The sorbents were obtained by post-crosslinking swollen styrene-divinylbenzene copolymers containing chloromethyl groups via Friedel-Crafts reaction. These sorbents do not contain any unintended functional groups capable of ion exchange. The content of residual chloromethyl and hydroxymethyl groups does not exceed 0.1 meq/g so that they do not play any noticeable role in separation of concentrated electrolytes.

Water pre-swollen beads of 0.3–0.5 mm in diameter were slurry packed in glass columns, mostly of 30 mL or 44 mL in volume (about 1 cm in diameter). In order to avoid tailing of chromatographic zones due to convective fluxes of a more dense (compared to water) solution of electrolytes, the latter was percolated through the column from its bottom upwards till the equilibration of the column with the feed solution completed. This experiment was called direct one. Afterwards, electrolytes were displaced from the column in opposite direction by the flow of pure water. This is reversed experiment. (In all figures the breakthrough curves resulting from direct experiments are separated by a gap from the elution part of the chromatograms). Under these conditions, the shape of fronts is determined only by the nonlinearity of phase distribution isotherms and longitudinal dispersion of concentration fronts. In the both direct and reversed experiments the effluent was collected in fractions of 1.2–1.5 mL. The flow rate was, on average, 1 mL/min. The concentration of electrolytes in each fraction of the effluent was then determined using appropriate volumetric analysis.

2.4 Dimensions of Hydrated Ions

To discuss the separation of electrolytes in frames of the ion size exclusion process, while accepting the idea that strong electrolytes completely dissociate into constituent ions, one needs to have information about the size of the individual ions in

Table 2.1 Hydration numbers of cations determined by different methods (Tanganov 2005)

Method of measurement	Hydration numbers of cations					
	Li ⁺	Na ⁺	K ⁺	Rb ⁺	Cs ⁺	NH ₄ ⁺
Electrophoretic mobility of ions	–	–	16	13	14	1
Self-diffusion coefficient	14	8.4	5.4	–	–	–
	–	–	22	–	–	–
	–	16.9	9.6	6.4	4.7	10.7
Rate of diffusion through membrane	5	3	4	–	–	–
Dependence of activity coefficient on concentration	7	3.5	1.9	1.2	–	–

Table 2.2 Hydration numbers of anions determined by different methods (Tanganov 2005)

Method of determination	Hydration numbers of anions			
	F [–]	Cl [–]	Br [–]	I [–]
Thermochemical method	–	4.4	4.8	5.3
Isothermal compression	4.5	2.0	1.8	1.5
Stoke's radius	5.5	3.9	3.4	2.8
NMR chemical shift	1.6	–1.1 ^a	–3.2 ^a	–7.5 ^a
NMR relaxation time	9.9	13.2	16.2	21.8
IR-spectroscopy	6.0	6.0	6.3	9.1
X-ray diffraction	4.5	6	6	8.8
Neutron scattering	–	5.8	–	–

^a Shift of the NMR signal to high field

aqueous media. There has been a great deal of debate for more than a century on the solvation of ions and the effect that dissolved ions have on the tetrahedral network structure of water. A central theme of that discussion has been the notion that different ions have “structure making” or “structure breaking” effects, depending on the charge and size of the ion. While potassium is regarded as being rather neutral in its effect on the structure of water (Hribar et al. 2002), the information collected so far for other mineral ions, even for the simplest ions, is very contradictory and inconclusive.

With respect to the number of water molecules comprising the hydration shell of an ion, static and dynamic methods of investigation show incompatible results. Static methods include thermochemistry (Samoilov 1957, 1972), NMR time relaxation (Fabricand and Goldenberg 1961), IR spectroscopy (Bergstrom et al. 1991), X-ray diffraction (Licheri et al. 1976; Biggin et al. 1984), or neutron scattering (Soper and Weckström 2006). These techniques provide information on the size of the hydration shell of ions in the bulk solution. Viscosimetric determination of the Stokes radius (Marcus and Solvation 1985), measuring isothermal compression of solutions (Bocris and Saluya 1972), the rate of ion migration through a membrane as well as ion self-diffusion coefficients (Pinto and Graham 2004) are considered as dynamic methods, which characterize the moving ions. Tables 2.1 and 2.2 demonstrate how the results of the above measurements are contradictory. Unfortunately, we cannot judge which of them are more or less trustworthy. For that reason in our work we have used the list for sizes of hydrated ions from published

Table 2.3 Crystal radii (r_{crist}) and effective radii of hydrated ions (r_{H}) (25 °C) (Nightingale 1959)

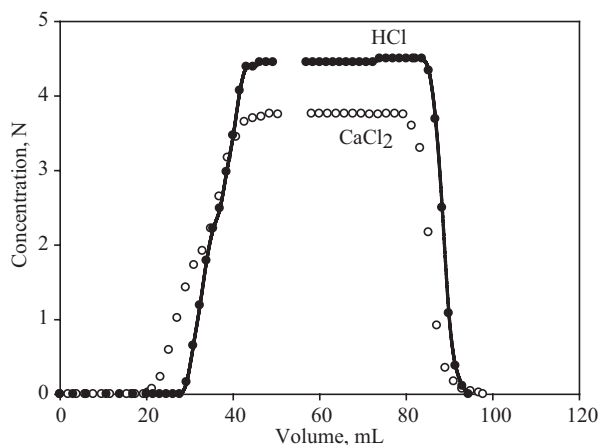
Ion	$r_{\text{crist}} \text{ \AA}$	$r_{\text{hydr}} \text{ \AA}$	Ion	$r_{\text{crist}} \text{ \AA}_t$	$r_{\text{hydr}} \text{ \AA}$
(Me) ₄ N ⁺	3.47	3.67	OH ⁻	1.76	(3.00)
(Et) ₄ N ⁺	4.00	4.00	F ⁻	1.36	3.52
(<i>n</i> -Pr) ₄ N ⁺	4.52	4.52	Cl ⁻	1.81	3.32
(<i>n</i> -Bu) ₄ N ⁺	4.94	4.94	Br ⁻	1.95	3.30
(<i>n</i> -Pe) ₄ N ⁺	5.29	5.29	I ⁻	2.16	3.31
H ⁺	(2.82)		NO ₃ ⁻	2.64	3.35
Li ⁺	0.60	3.82	ClO ₃ ⁻	2.88	3.41
Na ⁺	0.95	3.58	BrO ₃ ⁻	3.08	3.51
K ⁺	1.33	3.31	IO ₃ ⁻	3.30	3.74
Rb ⁺	1.48	3.29	ClO ₄ ⁻	2.92	3.38
Cs ⁺	1.69	3.29	IO ₄ ⁻	3.19	3.52
Ag ⁺	1.26	3.41	MnO ₄ ⁻	3.09	3.45
Tl ⁺	1.44	3.30	ReO ₄ ⁻	3.30	3.52
NH ₄ ⁺	1.48	3.31	CO ₃ ²⁻	2.66	3.94
Be ⁺⁺	0.31	4.59	SO ₄ ²⁻	2.90	3.79
Mg ⁺⁺	0.65	4.28	SeO ₄ ²⁻	3.05	3.84
Ca ⁺⁺	0.99	4.12	MoO ₄ ²⁻	3.23	3.85
Sr ⁺⁺	1.13	4.12	CrO ₄ ²⁻	3.00	3.75
Ba ⁺⁺	1.35	4.04	WO ₄ ²⁻	3.35	3.93
Ra ⁺⁺	1.52	3.98	Fe(CN) ₆ ⁴⁻	4.35	4.22
Mn ⁺⁺	0.80	4.38			
Fe ⁺⁺	0.75	4.28			
Co ⁺⁺	0.72	4.23			
Ni ⁺⁺	0.70	4.04			
Cu ⁺⁺	0.72	4.19			
Zn ⁺⁺	0.74	4.30			
Cd ⁺⁺	0.97	4.26			
Pb ⁺⁺	1.32	4.01			
Al ⁺⁺⁺	0.50	4.75			
Cr ⁺⁺⁺	0.64	4.61			
Fe ⁺⁺⁺	0.60	4.51			
La ⁺⁺⁺	1.15	4.52			
Ce ⁺⁺⁺	1.1	4.52			
Tm ⁺⁺⁺	0.9	4.65			
Co(NH ₃) ₆ ⁺⁺⁺	2.55	3.96			

work (Nightingale 1959). Since the radii of many hydrated cations and anions were estimated using measurements by the same method of electro conductivity, at least, their comparison is possible. Table 2.3 presents these values.

2.5 Separation of Electrolytes on Nanoporous Hypercrosslinked Sorbents

Owing to the high rigidity of the open-network structure of hypercrosslinked polystyrene, the latter is fully accessible to small analyte molecules not only in organic but also in aqueous media. Using this property of the hydrophobic nanoporous matrix, the behavior of inorganic electrolytes in a hypercrosslinked polystyrene matrix can

Fig. 2.1 Elution profiles for HCl and CaCl_2 (examined separately) from the chromatographic column containing NN-381. Experimental conditions: 44 mL column, 0.8 mL/min flow rate

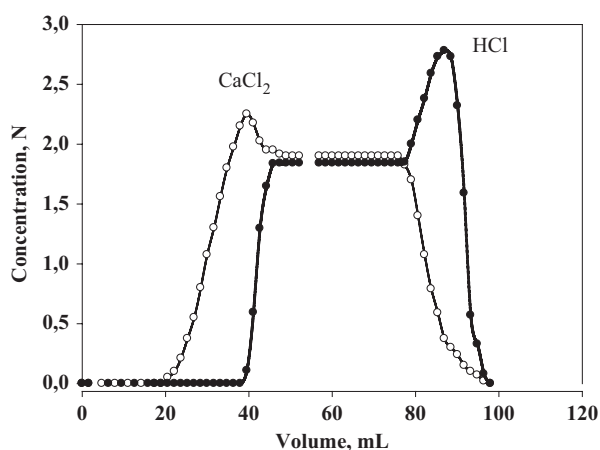


be studied. The column (44 mL) was filled with a suspension of 33.3 g water-swollen beads of sorbent NanoNet 381 in water. In this column, the interstitial volume amounts to 17.6 mL (40% of column volume, Manalo et al. 1959). Taking into consideration that one gram of the dry sorbent takes up 1.23 mL water, simple calculations show the total volume of water (mobile phase) in the column to be equal to 36 mL.

First of all, a 3.45 N solution of CaCl_2 was percolated through the column and then the salt was eluted with pure water. The same experiment was performed with 3.75 N solution of hydrochloric acid. Figure 2.1 demonstrates the trapezium-shaped combination of breakthrough and elution curves. In both the direct and reversed experiments the salt leaves the column sooner than the acid. Indeed, in the direct experiment the breakthrough of CaCl_2 occurs at 32.5 mL (measured at the center of concentration front) while the elution volume for HCl was 35.4 mL. The latter value practically equals the total volume of mobile phase in the column and so we have to arrive at the conclusion that, initially, the *neutral hypercrosslinked polystyrene sorbet NN-381* does not retain hydrochloric acid and practically all pores in the sorbent are accessible to the acid, while CaCl_2 is partially excluded from the finest pores. In this experiment the fronts of CaCl_2 and HCl diverged by 7% of bed volume.

The situation changes dramatically when a binary concentrated solution of CaCl_2 in HCl is pumped through the same column (Fig. 2.2). Now, CaCl_2 emerges from the column much earlier than in the first experiment (22.7 mL against 32.5 mL) while HCl, on the contrary, retards and comes out with 43 mL. It looks like NN-381 retains hydrochloric acid only from its mixture with CaCl_2 . In this chromatographic experiment with the binary solution the fronts of the two electrolytes are separated by one third of bed volume so that it is possible to get a fraction of pure CaCl_2 solution in the direct experiment and a fraction of HCl solution in the reversed experiment. The same good separations (sometimes even better) were obtained on percolating concentrated solutions of LiCl, KCl, FeCl_2 or MgCl_2 in concentrated hydrochloric acid. Moreover, in all cases an unusual fact engages our attention: the concentration of each separated component at column outlet exceeds their initial concentrations in the mixture.

Fig. 2.2 Elution profiles for HCl and CaCl_2 (taken as a mixture) from the chromatographic column containing NN-381. Experimental conditions: 44 mL column, 0.8 mL/min flow rate



However, prior to explaining the difference in the above-described experiments we should answer the main question: why does the non-functionalized hypercrosslinked polystyrene separate ions?

Due to the principle of local electroneutrality, cations move along the column together with their anions. In the aforementioned examples (Figs. 2.1 and 2.2), the salt and the acid have the same chloride-anions. In that case the divergence of the salt and acid fronts may be conditioned upon one of two reasons, namely, (i) either the neutral polystyrene sorbent retains protons of the acid more strongly than it retains cations of alkali and alkali-earth metals, or (ii) different portions of sorbent internal volume are accessible to the acid and salt, i.e., they are excluded from the sorbent phase to different extents. Actually, the interaction of cations (including protons) with aromatic structures is well known (Ma and Dougherty 1997; Mecozzi et al. 1996). In hypercrosslinked polystyrene these interactions can be even enhanced because of the presence of condensed aromatic structures. For instance, anthracene-like fragments may readily emerge due to condensation of two chloromethylated styrene monomers during the synthesis procedure, occasionally followed by oxidative dehydration. Though, the amount of such proton sorption sites could not be high.

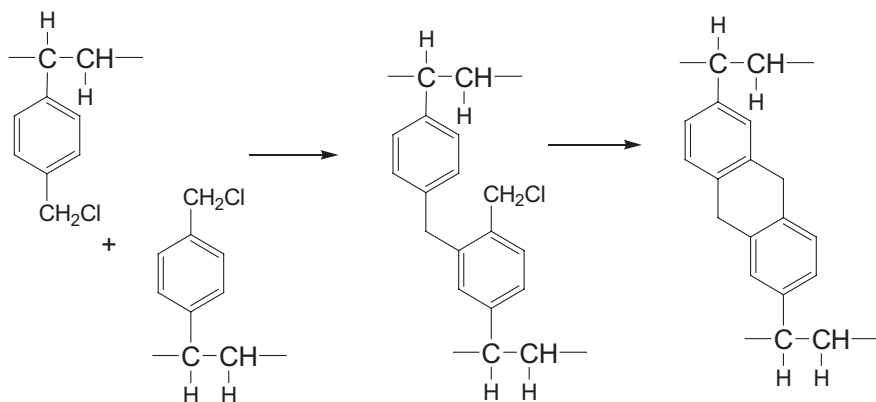


Table 2.4 Sorption of HCl, NaCl and NaOH on hypercrosslinked sorbent^a NanoNet 381

Sorbate	Initial concentration, meq/mL	Equilibrium concentration, ^b meq/mL
HCl	1.364	1.360
HCl	1.417	1.425
NaCl	1.568	1.682
NaOH	2.050	2.108

^a 50 g water-swollen sorbent, 100 mL solution, 3 days of periodical agitation at ambient temperature

^b Calculated with a glance of water added with swollen polymer sample

On the other hand, partial exclusion of hydrated ions seems to be unavoidable. In hypercrosslinked sorbent NN-381 about half of pores have diameter of 1.5 nm so that one may expect the presence of smaller pores, comparable with the size of hydrated inorganic ions.

If hypercrosslinked polystyrene exhibits enhanced affinity to protons, it should be evident not only under chromatographic (dynamic) conditions as the appearance of the acid breakthrough front behind the front of its salt and the front of mobile phase, but also under static conditions as an increase in the acid concentration in the sorbent phase (when the sorbent stands in contact with a solution of acid). In the latter case, acid concentration in the outer aqueous solution must decrease. Table 2.4 shows the results of experiments conducted under static conditions. As can be seen, *the hypercrosslinked sorbent does not retain hydrochloric acid* since its concentration in the supernatant did not change after long contact of NanoNet 381 with the acid solution. Contrary to this, the concentration of NaCl and NaOH in similar experiments increased compared to their initial concentration. This implies that, as opposed to HCl and water molecules, certain part of total pore volume is inaccessible to NaCl and NaOH. In other words *cations of the salt and the base are partially excluded from sorbent phase*.

Cations of alkali and alkaline-earth metals are highly hydrated in aqueous solutions and their dimensions exceed that of hydrated chloride-anions (Table 2.3). Hydroxonium ion (H_3O^+) should also be hydrated in aqueous solutions, but it can easily appear in any place where a molecule of water is present under condition that the latter is connected to continuous aqueous phase by hydrogen bridges. Therefore, under chromatographic conditions proton does not move along the column because very fast shift of electrons along the chains of hydrogen bonds (see scheme below) can provide any required redistribution of charges in the aqueous phase, thus imitating the movement of protons and/or hydroxyls. This effect is responsible for extremely high electrophoretic mobility of these ions in aqueous solutions, as well as high electro conductivity of aqueous solutions of acids and bases.

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