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Zwitterion-exchange properties of sulfonated hypercrosslinked polystyrene

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The simultaneous separation of nitrate, iodide, perchlorate, sodium, potassium and ammonium was achieved in 10 min on a column packed with spherical sulfonated hypercrosslinked polystyrene particles using 2.5 mM sulfuric acid.

A new polymeric material, so-called hypercrosslinked polystyrene (HCPS), is of interest as a stationary phase for HPLC.[1–3] HCPS has better mechanical properties than other polymers used in HPLC. High rigidity and a unique bimodal porous structure are typical of this material. Its swelling propensity in different organic solvents is comparable with that of silica-based materials rather than that of other polymer-based sorbents, which allows the use of a longer chromatographic column.[1]

Being a hydrophobic adsorbent, HCPS has a good wetting ability by water, and fine particles of HCPS can form a compact precipitate. It was found[2,3] that non-modified HCPS (a neutral polymer) exhibits strong anion-exchange ability towards inorganic anions. This property was attributed[4] to the presence of carbonyl groups at the surface of HCPS, which, under acid conditions, are protonated and can be responsible for the anion-exchange properties of HCPS.[2,3]

The incorporation of strongly acidic cation-exchange sulfo groups could provide zwitterionic properties to the resulting substrate due to the addition of negatively charged groups to positively charged carbonyls on the surface of starting HCPS. Similar approach to the design of zwitterion-exchangers was proposed by Dolgonosov,[5] who used partially sulfonated microparticles of a strongly basic anion exchanger as an efficient stationary phase for the separation of ions. Depending on the degree of sulfonation, the resulting material behaved as an anion, zwitterion or cation exchanger. Zwitterionic ion-exchangers are promising for ion-chromatographic analysis. This type of ion exchangers has advantages over traditionally used monofunctional ion exchangers. First, this unique ion-exchange selectivity allows simultaneous separation of both cations and anions on a single column with an eluent of constant composition.[6,7] The aim of this work was to study the ion-exchange properties of sulfonated HCPS with a low cation-exchange capacity. This material was originally used for the ion-exclusion chromatography of organic acids.[8]

The isocratic HPLC system consisted of a Model LC-10ATvp high-pressure pump (Shimadzu), a Model 7125 injection valve (Rheodyne) equipped with a 20 µl sample loop and a Conductolyzer 5300B conductometric detector (LKB). A stainless-steel (150×4.6 mm) column was slurry packed with sulfonated HCPS (3 µm, 0.07 mmol SO_3H groups g^{-1}).

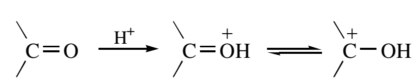
Table 1 The effect of the eluent on the retention factors (*k*) of ions on sulfonated HCPS. Eluents: 5 mmol dm^{-3} solutions of $MeSO_3H$, $HClO_4$, H_3PO_4 or HNO_3 and 2.5 mmol dm^{-3} solution of H_2SO_4.

Ion	H_2SO_4	$MeSO_3H$	$HClO_4$	H_3PO_4	HNO_3
Na^+	2.86	2.50	2.87	3.57	2.26
Li^+	3.26	2.65	3.18	3.92	2.39
K^+	4.03	3.31	3.87	4.89	2.99
Rb^+	5.04	4.05	4.62	5.94	3.61
NH_4^+	5.15	3.98	4.97	6.27	3.78
Cs^+	7.95	5.98	7.18	9.55	5.59
System peak	0.09	0.95	0.94	0.19	0.26
SO_4^{2-}	0.09	0.10	0.05	0.05	0.05
Cl^-	0.14	0.18	0.07	0.08	—
Br^-	0.19	0.22	0.09	0.19	—
NO_3^-	0.25	0.29	0.14	0.23	0.27
IO_4^-	0.41	0.58	—	—	—
I^-	0.59	0.73	0.29	0.51	0.43
ClO_4^-	1.23	1.49	0.95	0.95	1.42

Solutions of sulfuric, perchloric, methanesulfonic, nitric (all of analytical grade, Reakhim, Russia) and phosphoric acids (HPLC grade, Fisher, USA) in distilled water were used as eluents. Aqueous solutions (10 mmol dm^{-3}) of alkali metal salts were used as analytes.

The retention of inorganic cations and anions on sulfonated HCPS was studied with dilute inorganic acids as eluents (Table 1). The remarkable retention of both anions and cations was observed. According to the retention times, the power of acids increases in the order $H_3PO_4 < HClO_4 < H_2SO_4 < MeSO_3H < HNO_3$ (the elution of cations) or $MeSO_3H < H_2SO_4$, $HNO_3 < H_3PO_4 < HClO_4$ (the elution of anions). Sulfuric acid solutions (0.5–10 mmol dm^{-3}) were used.

The effect of sulfuric acid concentration on retention was studied for inorganic cations (Li^+, Na^+ and K^+) and anions (Cl^-, NO_3^-, I^-, ClO_4^- and CNS^-) (Figure 1). As it was expected, the retention of cations increased and that of anions decreased with eluent concentration. The obtained retention order of cations was unusual for strong cation exchangers ($Na^+ < Li^+ < K^+ < Rb^+ < NH_4^+ < Cs^+$, in particular, a stronger retention of Li^+ and NH_4^+). This phenomenon can be explained by a matrix effect. HCPS contains about 6 mass% oxygen,[4] which can be attributed to the presence of carbonyl and hydroxy groups at the surface, as well as in micropores. Note that HCPS has a biporous structure consisting mainly of micropores (< 1 nm in diameter).[1] The presence of oxygen-containing functional groups in the micropores makes possible a multiple coordination of Li^+ and NH_4^+ by these groups. However, the bare HCPS does not show any ability to retain cations. This is due to the repulsion of cations from the positively charged surface of non-modified HCPS. It was assumed[2,3] that the protonation of carbonyl groups is responsible for the existence of a positive charge at the surface, as well as for the anion-exchange ability of HCPS itself:



$$\mathrm{>C{=}O \xrightarrow{H^+} >C{=}\overset{+}{O}H \rightleftharpoons >\overset{+}{C}{-}OH}$$

Thus, only the joint presence of sulfo and protonated carbonyl groups produces such a type of cation-exchange selectivity for sulfonated HCPS. The same selectivity was found earlier[9] for HCPS impregnated with methyl orange.

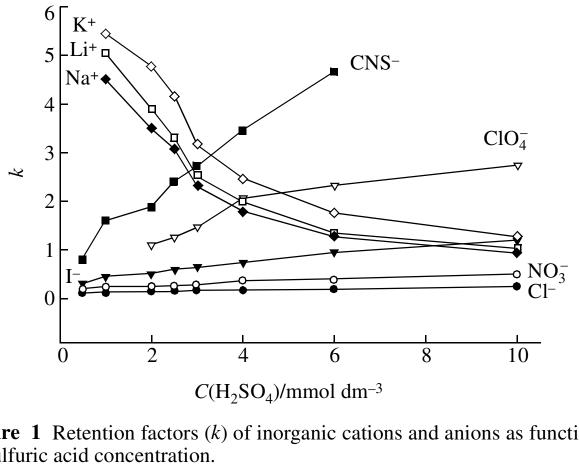


Figure 1 Retention factors (*k*) of inorganic cations and anions as function of sulfuric acid concentration.

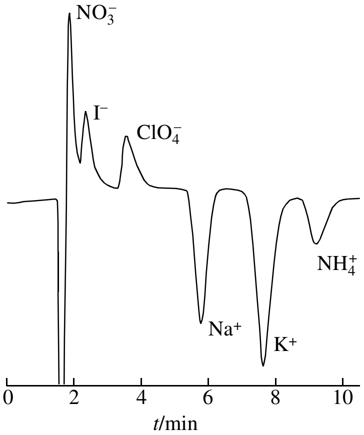


Figure 2 Simultaneous separation of a test mixture of inorganic anions and cations. Column: sulfonated HCPS, 3 μm, 150×4.6 mm. Eluent: 2.5 mmol dm^{-3} H_2SO_4. Flow rate, 1 ml min^{-1}. Detection: conductometric.

The similar selectivity was noted for the retention of alkali metal cations on sulfonated PS-DVB resin in a 2-methylpyridine-based eluent.[10] Several aromatic bases were studied as eluents but only sterically hindered alkylpyridines produced such a cation-exchange selectivity. Taking into consideration the strong retention of 2-methylpyridine, its high hydrophobicity a dynamic modification of low-capacity strong cation-exchanger with alkylpyridines was possible. Thus, the combination of positively and negatively charged groups could be responsible for the resulting selectivity.

The dependence of the retention factors of anions on the concentration of sulfuric acid (Figure 1) on sulfonated HCPS has no maximum, which was obtained for bare HCPS. The increase of eluent concentration up to 10 mmol dm^{-3} leads to the domination of anion-exchange properties due to protonation of residual carbonyls at the surface of sulfonated HCPS in accordance with the above scheme. The retention order of anions on sulfonated HCPS ($SO_4^{2-} < Cl^- < Br^- < NO_3^- < IO_4^- < I^- < ClO_4^- < CNS^-$) corresponds to that observed with non-modified HCPS except for IO_4^- and SO_4^{2-}, which are weaker retained on sulfonated HCPS.[3] The weak retention of the SO_4^{2-} anion is common for zwitterion exchangers, and it can be explained by the repulsion from negatively charged sulfo groups in sulfonated HCPS.[6] The increase in the eluent ionic strength or injected sample ionic strength causes a decrease in the retention times of both cations and anions without significant changes in separation selectivity.

The simultaneous separation of NO_3^-, I^- and ClO_4^- anions and Na^+, K^+ and NH_4^+ cations with 2.5 mmol dm^{-3} sulfuric acid solution on sulfonated HCPS was achieved in 10 min (Figure 2). The number of theoretical plates was about 7500–8900 for alkali metal cations. The efficiency of 150 mm column was insufficient for the separation of more ions.

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References

1 N. A. Penner, P. N. Nesterenko, M. M. Ilyin, M. P. Tsyurupa and V. A. Davankov, *Chromatographia*, 1999, **50**, 611.

2 N. A. Penner and P. N. Nesterenko, *Anal. Commun.*, 1999, **36**, 199.

3 N. A. Penner and P. N. Nesterenko, *J. Chromatogr. A*, 2000, **884**, 41.

4 M. Streat and L. A. Sweetland, *Trans. Inst. Chem. Eng.*, 1998, **76**, 115.

5 A. M. Dolgonosov, *J. Chromatogr.*, 1994, **671**, 33.

6 P. N. Nesterenko and P. R. Haddad, *Anal. Sci.*, 2000, **16**, 565.

7 P. N. Nesterenko, D. A. Tarasenko and O. A. Shpigun, *Zh. Anal. Khim.*, 1994, **49**, 244 [*J. Anal. Chem.* (*Engl. Transl.*), 1994, **49**, 222].

8 P. N. Nesterenko, P. A. Kebets and Yu. V. Volgin, *Zh. Anal. Khim.*, 2001, **56**, 801 [*J. Anal. Chem.* (*Engl. Transl.*), 2001, **56**, 715].

9 M. G. Kiseleva, L. V. Radchenko and P. N. Nesterenko, *J. Chromatogr. A*, 2001, **920**, 79.

10 P. R. Haddad and R. C. Foley, *Anal. Chem.*, 1989, **61**, 1435.

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