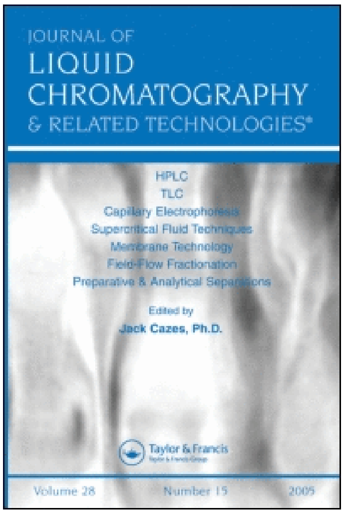

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SURFACE SULFONATED STYRENE DIVINYL BENZENE-OPTIMIZATION OF PERFORMANCE IN ION CHROMATOGRAPHY

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ABSTRACT

When used with Ion Chromatography as a pellicular cation-exchanger, the optimum performance capacity of 50μ surface sulfonated styrene 2% divinyl benzene copolymer was found to be about 0.018 meq/g. This observation was at great variance with the theory and was explained by much slower diffusion of cations in this ion-exchanger relative to fully sulfonated ones. Slower diffusion was attributed to hindered swelling of the sulfonated polymer on the unsulfonated core and to varying percent sulfonation within the sulfonated region.

INTRODUCTION

The use of surface sulfonated styrene divinyl benzene copolymer (SS-SDVB) as a "pellicular" ion-exchanger for chromatography was first demonstrated by Pepper,(1) and then by Parrish.(2) This work was done about twenty years ago and until a recent article by Hansen and Gilbert(3) little else about SS-SDVB is found in the published literature. The main interest of other workers has been to coat an impervious core with ion-exchanger. Horvath, et al,(4) described a method of coating glass beads with a crosslinked polystyrene pellicle and then sulfonated the pellicle to produce a strong acid pellicular ion-exchanger. Kirkland(5) impregnated a surface porous layer bead with sulfonated fluoropolymer to produce ZIPAX SCX† chromatographic packing. Battaerd, et al, described a method of graft polymerization of α-olefins, carrying a sulfonic acid group, on a core of a polyolefin material(6).

Hansen and Gilbert(7) modified the classical Glueckhauf equation to apply to pellicular ion-exchangers. They concluded that the optimum pellicle depth for SS-SDVB would be about 7000 Å for a 60μ bead diameter.

We have experimentally determined the optimum pellicle depth of SS-SDVB as well as the optimum composition of crosslinking agent in the copolymer(8) and found our results in great variance with present theory when SS-SDVB was used in "Ion Chromatography".

Ion Chromatography is a new analytical technique using two ion-exchange columns in series followed by a flow-through electrical conductivity detector. The first column (called the analytical column) separates the ions in the injected sample, while the second column (called the stripper column) suppresses the conductance of the electrolyte in the eluent but not that of the separated ions.(10) The subject of this contribution is the experimental determination of the optimum sulfonation depth and percent crosslinking agent and our explanation of the variance between the theoretical and actual optimum observed when SS-SDVB is used in Ion Chromatography.

SS-SDVB outperformed ZIPAX SCX Chromatographic Packing, HS PELLIONEX+ SCX Chromatographic Packing and HC PELLIONEX+ SCX Chromatographic Packing when used in Ion Chromatography.(8)

EXPERIMENTAL

The Ion Chromatograph used was a pre-production prototype of the Model 10 unit available from Dionex Corporation, 1228 Titan Way, Sunnyvale, California, 94086. The eluent used was 0.01 M nitric acid in deionized water. The flow rate varied from 46 to 460 ml/hr. The analytical column dimensions were either 2.8 x 300 mm or 9 x 125 mm and these columns were packed with SS-SDVB. The stripper column dimensions were either 2.8 x 300 mm or 9 x 250 mm and these columns were packed with DOWEX* 1 x 10 ion exchange resin in the hydroxide ion form. Detector sensitivity was set at 10μ mho cm^{-1} full scale.

The SS-SDVB was prepared by the method outlined in reference 10.

RESULTS AND DISCUSSION

Data Treatment

Various compositions of SS-SDVB were evaluated on the basis of the chromatographic resolution attained between 1.1 microgram of sodium ion and 3.4 microgram of potassium ion, Figure 1. The data were obtained from chromatograms by triangulating the sodium and potassium peaks to the base-line and measuring in ml, the peak, widths, W_k and W_{Na}. Resolution observed, R_o, was then calculated according to the following equation, where S is the peak to peak separation in ml.

Equation 1: $$R_o = \frac{S}{(W_k + W_{Na})\ 1/2}$$

To appropriately compare the various SS-SDVB compositions the R_o data was transformed to give a transformed resolution, R_{TR}, as if the separation were 4 ml, see equation 2.

Equation 2: $$R_{TR} = \frac{4\ R_o}{S}$$

$$R_O = \frac{12.3}{(4.60 + 7.67)½} = 2.00$$

$$R_{TR} = \frac{\sqrt{4}\,2.00}{\sqrt{12.3}} = 1.14$$

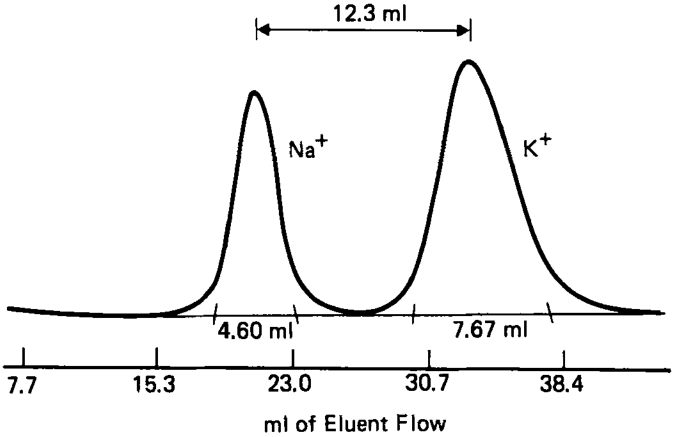

FIGURE 1

EXAMPLE CHROMATOGRAM AND CALCULATIONS

An evaluation of various SS-SDVB compositions was then made based on the criteria that higher R_{TR} gave better performance.

Percent Crosslinking

Table 1 lists the chromatographic data for SS-SDVB ranging from 0.04 to 12 percent crosslinking with capacity held to 0.025 ± 0.005 meq/g using a 2.8 x 300 mm analytical column and a 9 x 250 mm stripper column. Figure 2 is a plot of R_{TR} vs. % crosslinking. The optimum divinylbenzene composition of SS-SDVB is about 2%.

TABLE 1

Run No.	Elution Speed (cm/min)	S (ml)	R_O	if S were	R_{TR}* would be
1a	15.6	1.44	0.72	4 ml	1.20
2a	15.6	2.59	1.69	"	2.10
2b	31.2	2.67	1.59	"	1.95
2c	62.3	2.68	1.40	"	1.71
3a	15.6	2.40	1.67	"	2.16
3b	31.2	2.50	1.68	"	2.13
3c	62.3	2.53	1.57	"	1.97
4a	15.6	3.36	1.59	"	1.73
4b	31.2	3.30	1.51	"	1.66
4c	62.3	3.37	1.43	"	1.56
5a	15.6	2.74	0.88	"	1.06
5b	31.2	2.80	0.80	"	0.96
5c	62.3	2.76	0.72	"	0.87
6a	15.6	2.11	0.79	"	1.09
6b	31.2	1.97	0.79	"	1.13
6c	62.3	1.95	0.78	"	1.12

Run 1 - 0.04% X-link; ∿50μ bead size (230-325 U.S. mesh); ∿280 Å sulfonation depth** (0.030 meq/g)
Run 2 - 2% X-link; ∿50μ bead size (230-325 U.S. mesh); ∿205 Å sulfonation depth** (0.022 meq/g)
Run 3 - 2% X-link; ∿50μ bead size (230-325 U.S. mesh); ∿215 Å sulfonation depth** (0.023 meq/g)
Run 4 - 4% X-link; ∿50μ bead size (230-270 U.S. mesh); ∿235 Å sulfonation depth** (0.025 meq/g)
Run 5 - 8% X-link; ∿50μ bead size (320-325 U.S. mesh); ∿190 Å sulfonation depth** (0.020 meq/g)
Run 6 - 12% X-link; ∿50μ bead size (320-325 U.S. mesh); ∿205 Å sulfonation depth** (0.022 meq/g)
*Calculated from Equation 2 **Calculated from Figure 3

Calculated Sulfonation Depth

If the assumption is made that SS-SDVB is composed of a 100% sulfonated surface layer on an unsulfonated core then sulfonation depth can be calculated from the exchange capacity of SS-SDVB and the bead diameter. Figure 3 is a family of curves of calculated sulfonation depth vs. capacity in meq/g for various bead dia-

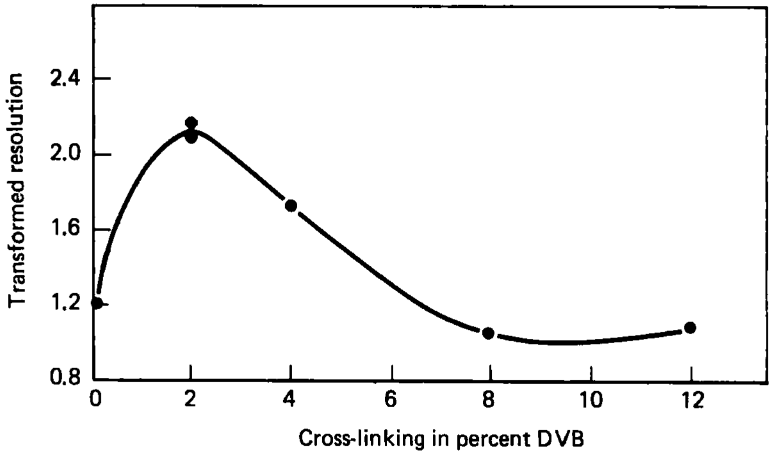

FIGURE 2

OPTIMUM PERCENT DIVINYLBENZENE IN SURFACE SULFONATED STYRENE DIVINYLBENZENE

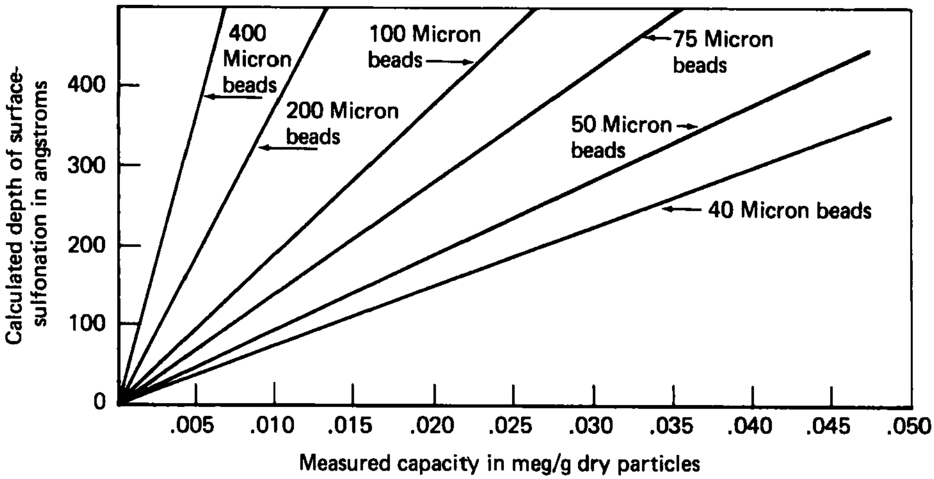

FIGURE 3

CALCULATED SULFONATION DEPTH vs CAPACITY FOR SURFACE SULFONATED STYRENE DIVINYLBENZENE

meters for SS-SDVB. Table 2 and Figure 4 lists chromatographic data for 2% DVB SS-SDVB of about 50μ bead diameter (230-350 US mesh) with calculated sulfonation depths varying from about 95 Å to 440 Å using a 9 x 125 mm analytical column and a 9 x 250 mm stripper column.
A calculated sulfonation depth up about 175 - 200 Å is optimum even though lower depth of sulfonation give similar R_{TR} because columns packed with lower capacity exchanger would have to be longer to obtain equivalent actual resolutions. Longer columns would require higher pressures or if pressure is limited, longer analysis time..

TABLE 2

Run No.	Elution Speed (cm/min)	S (ml)	R_O	if S were	R_{TR}* would be
7a	12.1	4.88	1.63	4 ml	1.48
7b	6.0	4.49	1.97	"	1.86
8a	12.1	11.8	2.55	"	1.48
8b	6.0	11.2	3.08	"	1.84
9a	12.1	15.4	2.63	"	1.34
9b	6.0	14.9	3.15	"	1.63
10a	12.1	21.5	3.10	"	1.34
10b	6.0	21.0	3.39	"	1.48
11a	12.1	32.9	3.45	"	1.20
12a	12.1	42.8	3.36	"	1.03

Run 7 - Sulfonated 1 min at 90°C;
∿95 Å sulfonation depth** (0.010 meq/g)
Run 8 - Sulfonated 2 min at 90°C;
∿170 Å sulfonation depth** (0.018 meq/g)
Run 9 - Sulfonated 1 min at 100°C;
∿220 Å sulfonation depth** (0.023 meq/g)
Run 10- Sulfonated 4 min at 90°C;
∿265 Å sulfonation depth** (0.028 meq/g)
Run 11- Sulfonated 1.5 min at 100°C;
∿350 Å sulfonation depth** (0.037 meq/g)
Run 12- Sulfonated 8 min at 90°C;
∿440 Å sulfonation depth** (0.047 meq/g)
*Calculated from Equation 2 **Calculated from Figure 3

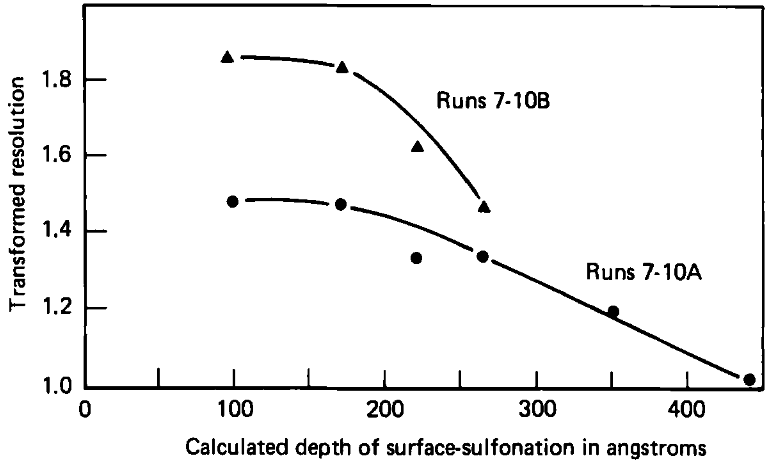

FIGURE 4

OPTIMUM SULFONATION DEPTH OF SURFACE SULFONATED STYRENE DIVINYLBENZENE

Comparing Theory with Practice

Hansen and Gilbert rigorously developed the theory of pellicular ion-exchange chromatography.(7) They concluded that for SS-SDVB the optimum pellicle depth would be about 7000 Å for a 60 micron bead radius.

We have determined that the actual optimum pellicle depth under those conditions is about 200 Å, and that the optimum divinyl benzene (DVB) crosslinking composition of SS-SDVB is about 2%. The D_s (diffusion of solute in the ion-exchanger) value of 2×10^{-7} cm^2/sec, used by Hansen and Gilbert, is the value reported in the literature for conventional ion-exchangers. An optimum pellicule depth of about 200 Å would have been predicted if a D_s value of 1×10^{-11} cm^2/sec was used.

In other words, theory and practice will agree if diffusion of solutes in the ion-exchanger (D_s) is much slower than for conventional exchanger.

Slower diffusion in the pellicle of SS-SDVB could be explained by two factors. The first is that the pellicle of ion exchanger is intimately bound to the core of the bead and thus could not swell as freely as a homogeneously sulfonated conventional exchanger. The hindered swelling would be similar to increased crosslinking and would decrease the diffusion rate.(9) Second, the sulfonation process probably does not produce a fully sulfonated pellicle on an impervious core, but probably produces a profile of decreasing percent sulfonation within the pellicle. Diffusion of cations in a partially sulfonated region would be slower than in a fully sulfonated one. Thus, D_s probably varies with pellicle depth because of hindered swelling and varying percent sulfonation.

"Pellicular" anion-exchangers have been made by us that overcame these difficulties. Approximately 10,000 Å DOWEX* 2 x 8 ion exchange resin was agglomerated onto the surface of 70 micron SS-SDVB.(10) The DOWEX* 2 x 8 ion exchange resin is free to swell and contains active ion-exchange groups homogeneously throughout the microbead. The experimentally determined optimum "pellicle depth" of this exchanger agreed with that predicted by Hansen and Gilbert's theory. Here, there probably is no significant difference between diffusion rates in the "pellicle" and for conventional DOWEX* 2 x 8 ion exchange resin.

CONCLUSION

The theoretical model of surface sulfonated styrene divinyl benzene proposed by Hansen and Gilbert will agree with experimental results if the diffusion of ions in the pellicle is much slower than the diffusion of ions in conventional homogeneously sulfonated exchanger. The optimum pellicle thickness for surface sulfonated styrene divinyl benzene prepared by conventional techniques, is about 200 Å for 50μ beads (capacity equal to about 0.018 meq/g) and the optimum DVB composition is about 2%.

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