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Effect of resin sulfonation on the retention of polar organic compounds in solid-phase extraction

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Abstract

The hydrophobic nature of polymeric resins used in solid-phase extraction (SPE) often limits their efficiency by preventing intimate surface contact with aqueous samples. A polymeric resin modified by a series of chemical derivatizations with sulfuric acid was found to display excellent surface hydrophilicity and improved extraction efficiencies. The degree of sulfonation was found to play a vital role in determining the SPE efficiency of such resins. By measuring the capacity factor of several polar organic solutes in pure water, an optimum sulfonation capacity of 0.6 mequiv./g was determined. Loose sulfonated resin and Empore membranes embedded with sulfonated resin were used for SPE. Average recoveries were greater than 95% for both types of sulfonated resin for a wide variety of organic compounds including phenols, alcohols, nitro compounds, aldehydes, esters and halogenated alkanes. Breakthrough curves for *p*-cresol, ethyl acetoacetate, isophorone and nitrobenzene were used to compare Empore membranes embedded with sulfonated and unsulfonated resin. The sulfonated membrane yielded sharper and more efficient breakthrough for all compounds tested.

1. Introduction

Sample preparation has been identified as often the slowest and therefore the most expensive step in the analytical process [1]. Solid-phase extraction (SPE) has become the preferred technique for sample preconcentration. Being a multi-stage method it is more efficient than simple liquid–liquid extraction. Analytes undergo multiple equilibrations with the resin and are therefore more strongly retained than in simple liquid extraction where only a single equilibration occurs. It is also more easily automated and much less polluting than liquid extraction techniques that often use relatively large volumes of organic solvents [2]. An early comprehensive paper investigated thoroughly the technique, scope, and limitations of SPE with porous polymeric resins (Rohm & Haas, XAD) [3]. Several reviews on SPE have been published [4,5]. Bonded-phase silica particles (mostly C_{18}- or C_8-) dominate the field, although porous polystyrene resins are finding increasing use because of their efficiency, ruggedness, and broader pH range.

One problem with extraction materials now used is the inability of aqueous solutions to adequately wet their surface, which is usually hydrophobic. This is true for both C_{18}-modified resin and underivatized polystyrene–divinylbenzene (PS–DVB). Pretreatment of the resin column or cartridge with methanol is usually necessary to obtain better surface contact with the aqueous solution [6,7].

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Recently it has been shown that introduction of polar groups into a PS–DVB resin greatly increases the retention of polar organic compounds. Sun and Fritz [6] modified PS–DVB with alcohol and acetyl functional groups. These modified resins exhibited excellent hydrophilicity and a lesser dependence on wetting prior to extraction. They also yielded higher recoveries compared to their unmodified analogue. This was attributed to an increase in surface polarity allowing the aqueous sample to make better contact with the resin surface. Schmidt and Fritz [8] used a sulfonated PS–DVB resin for the simultaneous extraction of bases and neutrals. Bases bind via ion exchange and neutrals by hydrophobic interactions. A two-step elution was then used to elute the bases and neutrals sequentially. Excellent recovery of both bases and neutrals was obtained. Mills et al. [9] recently compared sulfonated and unsulfonated C_{18}-modified resins for the extraction of triazine compounds. Once again, higher recoveries were obtained with the sulfonated resin. This was not attributed to the increased resin hydrophilicity but to hydrogen bonding between the amine functionality of the analytes and the sulfonic acid group on the resin. They also determined distribution coefficients (K_D) for the atrazine compounds on both resins, and found much high values for the sulfonated resins.

It is now shown that porous PS–DVB resins modified with surface sulfonic acid groups are superior to the unmodified PS–DVB for SPE of organic solutes from aqueous samples. However, the extent of the sulfonation is critical in determining extraction efficiency of such resins. The modified resins can be used for SPE in either of two modes: resin packed into mini columns or disks of resin-loaded membranes.

2. Experimental

2.1. Reagents and chemicals

Chemicals used for the sulfonation reactions were of reagent grade. All analytes studied were >99% pure and used as obtained from Aldrich and Fischer. Distilled water was further purified with a Barnstead Nanopure II System (Sybron Barnstead, Boston, MA, USA).

Several sulfonated resins were prepared from 8-μm PS–DVB obtained from Sarasep (Santa Clara, CA, USA). General reaction conditions are shown in Table 1. Specifically, 2 g of resin were mixed with 5 ml glacial acetic acid to form a slurry. Concentrated sulfuric acid was added with stirring. After a given reaction time, the mixture was quickly added to ice water to quench the sulfonation reaction. The resin was then filtered through a medium glass frit, and rinsed with deionized (DI) water, methanol, 2-propanol and finally acetone. After drying, the cation-exchange capacity was determined. A 1-ml volume of 1 *M* HCl was passed through a known amount of resin to ensure all exchange sites were protonated. After rinsing with DI water to remove excess HCl, 5 ml of a standardized NaOH solution were slowly passed through the column and collected into a flask containing 10 ml of a standard HCl solution. Following another DI water rinse, this was titrated with NaOH to the phenolphthalein endpoint. Capacities were calculated as milliequivalents SO_3^- per gram of resin.

2.2. Determination of k'

A small (20 × 2.1 mm I.D.) guard column (Supelco, Bellefonte, PA, USA) was filled with

Table 1
General reaction conditions for resin sulfonation

Capacity (mequiv./g)	H_2SO_4 (ml)	Reaction time (min)	Temperature
0.0			
0.1	5	0.5	Ice
0.4	50	2	Ice
0.6	50	4	Ice
1.0	50	10	Room temp.
1.2	50	20	Room temp.
1.5	50	90	Room temp
2.1	50	90	50°C
2.7	50	90	85°C

approximately 20 mg of resin. This guard column was contained within a guard column holder and connected to the HPLC system via two injection loops; a 10-μl loop from the injector (Rheodyne, Berkeley, CA, USA) and a 50-μl loop to the detector. The HPLC system consisted of a Gilson (Middleton, WI, USA) Model 302B HPLC pump equipped with a Model 802B Gilson manometric module and Scientific Systems (State College, PA, USA) Model LP-21 pulse dampener and a Kratos 783 UV–Vis detector (Applied Biosystems, Ramsey, NJ, USA). Retention times were measured with a Hitachi D-2000 Chromato-Integrator (EM Science, Cherry Hill, NJ, USA).

Samples (50 ppm, w/w) were prepared by diluting stock solutions in DI water. Depending on the absorbance of the analyte, 10–50 μl were injected. Phenols were detected at 270 nm and the carbonyl compounds at 205 nm. DI water at 0.5 ml/min was used as the eluent. The column dead time, t_0 was determined using the retention time of bromide (sodium bromide). This value included the travel time through the tubing (60 μl total volume); therefore 0.12 min was subtracted from the measured time to calculate the true t_0. This value was also subtracted from all analyte retention times.

Capacity factors were determined for the unwetted and methanol wetted resin. Wetting was accomplished by injecting two successive portions of methanol from a 500-μl loop, followed by a 4-ml rinse with DI water. During the water rinse the 500-μl injection loop was replaced with the smaller loop for sample injection.

2.3. Procedure for SPE

The apparatus for SPE consisted of a 30-ml glass syringe barrel fitted with a luer tip. A 1.5-ml polypropylene SPE column (P.J. Corbert Assoc., St. Louis, MO, USA) was connected to the glass reservoir via a universal adapter. Loose 8-μm sulfonated resin and Empore (3M Co., St. Paul, MN, USA) membranes embedded with sulfonated resin were used as the SPE adsorbents. This was placed between two 20-μm polyethylene frits (P.J. Corbert Assoc.) in the column. The bed height measured approximately 1 cm. Positive pressure was used to force liquids through the adsorbents. Prior to use, about 1 ml methanol and 2 ml water were used to rinse the column.

Samples were prepared by adding a 100-μl aliquot of a 150-ppm methanol solution containing 5–10 analytes to 15 ml of DI water. The final concentration of each compound in the sample was about 1 ppm. Air pressure was adjusted to provide a flow of 1–2 ml/min (30–60 p.s.i.; 1 p.s.i. = 6894.76 Pa). After loading, the glass reservoir was rinsed with 3–5 ml water and air was blown through the column to remove any remaining water. A 1-ml volume of ethyl acetate or methanol was used to elute the compounds into a GC vial. An internal standard (100 μl of a 150-ppm toluene solution in methanol) was added to the vial, which was then analyzed by gas chromatography. A Shimadzu (Kyoto, Japan) GC 14A equipped with an AOC-14 autoinjector, flame ionization detector and a C-R4A Chromatopac data analysis system was used to separate and quantitate the analytes. The GC column was a 15-m SPB-5 (Supelco) column. Recoveries were calculated as an average of three trials by comparing the relative peak areas with standards that were not subjected to SPE.

2.4. Breakthrough curve procedure

Breakthrough curves on a 46-mg sulfonated Empore membrane and a 44-mg unsulfonated Empore membrane were determined by passing a dilute solution (5–10 ppm) of analyte continually through the SPE column. Fractions of 5 or 10 ml were collected in volumetric flasks. In order to concentrate the analyte, the collected sample was passed through another sulfonated Empore membrane, which was eluted with 1 ml of methanol into a GC vial. After addition of the internal standard, the analyte concentration was determined by GC. Fractions were collected until the concentration of analyte remained constant.

3. Results and discussion

3.1. Sulfonation of resins

Our goal was to make the resin surface more hydrophilic while keeping the interior surface hydrophobic enough to allow extraction of organic solutes. A fairly rapid sulfonation with sulfuric acid seemed appropriate to accomplish this because sulfonation of resins is known to proceed from the outside into the resin. Reacting for a short time will therefore only modify the surface of the resin bead. In order to achieve more even wetting of the resin with viscous conc. sulfuric acid, the resin was first slurried with a little glacial acetic acid. Acetic acid has both a hydrophobic ($-CH_3$) and hydrophilic (–COOH) portion. This aids in contacting the polar acid and non-polar resin. Without the acetic acid the resin sits on surface of the sulfuric acid and does not react well.

Porous PS–DVB resin beads (average 8 μm) were sulfonated under a variety of conditions to produce sulfonated resins ranging in capacity from 0.1 to 2.7 mequiv./g. The sulfonation conditions and capacities are given in Table 1.

3.2. Measurement of k'

The efficiency of resins used for SPE is most commonly determined by measuring the percentage recovery of test solutes. However, this process depends on the efficiency of elution of the analytes from the SPE column as well as the efficiency of the initial extraction step. Laconto [5] has pointed out that for 90% recovery the K_D for the extraction step may be anywhere between 10 and 100. A better way to compare the behavior of different resins is to measure the capacity factor of the extraction step. Several methods have been used to measure k' in aqueous solutions. One common method for measuring capacity factors consists of measuring k' vs. φ, the percentage of organic solvent in the eluent. After obtaining several points, an extrapolation to 0% organic solvent is possible. Although this is a common procedure [10], it may not be the most accurate for SPE where aqueous samples are used. Surface modifications are undoubtedly taking place due to adsorption of some of the organic portion of the eluent onto the resin surface. It is better to determine k' in the same sample matrix that is common for SPE samples: 100% water. However, this can be difficult when k' is very large. Mills et al. [9] equilibrated a spiked aqueous sample with resin for 24 h. The analyte concentration remaining in the aqueous solution was used to calculate the equilibrium constant.

In the present work the k' values of various analytes were determined by elution from a very small resin column using pure water as the eluent. The method is quick and convenient and requires no extrapolation since no organic modifier is used in the eluent. The capacity factor is determined from the recorded elution curve using the well-known relationship: $k' = (t_R - t_0)/t_0$. In order for this method to be feasible, the column must be small; otherwise, many hours may be required for elution with water as the eluent. The values of k' are also dependent on the measured t_0, although an error in t_0 will still give relative values of k' that can be compared for different resins. Details of this method are given in the Experimental section.

Even with a small column non-polar compounds such as benzene would be retained for several hours and give flat elution "peaks". For this reason more polar, water-soluble compounds were chosen as test materials: phenol, catechol, 2,3-butanedione and ethyl pyruvate. These compounds are polar enough to elute in a reasonable time and are easily detected by a UV–Vis detector.

The k' values of these four test compounds are given in Table 2 and are plotted against the sulfonic acid capacity of the resins in Figs. 1 and 2. In each case the k' increases with increasing sulfonation capacity, reaching a maximum at about 0.6 mequiv./g. Further increases in sulfonic acid capacity are marked by a rapid decrease in k'.

The increasing k' values up to 0.6 mequiv./g can be attributed to the fact that a surface-sulfonated resin is more hydrophilic and therefore more easily wettable. The ability of water to

Table 2
Effect of sulfonation capacity on the retention of polar organic solutes in 100% water

Sulfonation capacity (mequiv./g)	Capacity factor							
	Phenol		Catechol		Ethyl pyruvate		2,3-Butanedione	
0.0	**49**	21	**10**	1	**0**	0	**1**	1
0.1	**124**	40	**32**	1	**4**	0	**2**	0
0.4	**350**	272	**45**	34	**49**	40	**4**	3
0.6	**457**	436	**90**	74	**79**	60	**14**	12
1.0	**381**	315	**70**	59	**55**	54	**8**	8
1.2	**324**	290	**78**	56	**57**	38	**7**	7
1.5	**209**	183	**45**	38	**34**	26	**6**	6
2.1	**127**	80	**25**	16	**16**	9	**4**	3
2.7	**55**	47	**12**	10	**6**	5	**2**	2

Values are averages of two trials. Bold numbers refer to methanol-wetted resins.

come into intimate contact with the resin surface facilitates the transfer of analyte from the aqueous sample to the resin surface. The wettability of a resin may be quickly checked by adding a few milligrams of dry resin to water. Hydrophobic resins will remain on the surface of the water even if stirred. Hydrophilic resins will be dispersed throughout the solution because of the ability of polar surface to reduce the surface tension of the water, thus allowing water to closely approach the resin surface. In terms of capacity, 0.6 mequiv./g is the minimum sulfona-

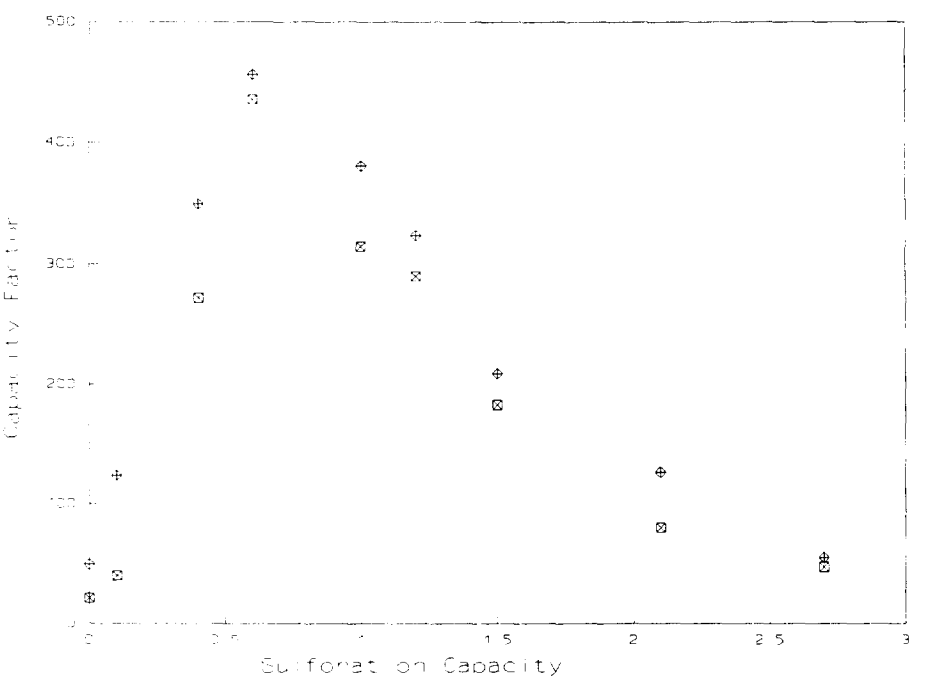

Fig. 1. Effect of PS–DVB sulfonation capacity (in mequiv./g) on retention of phenol in pure water for methanol wetted (◇) and unwetted (□) resins.

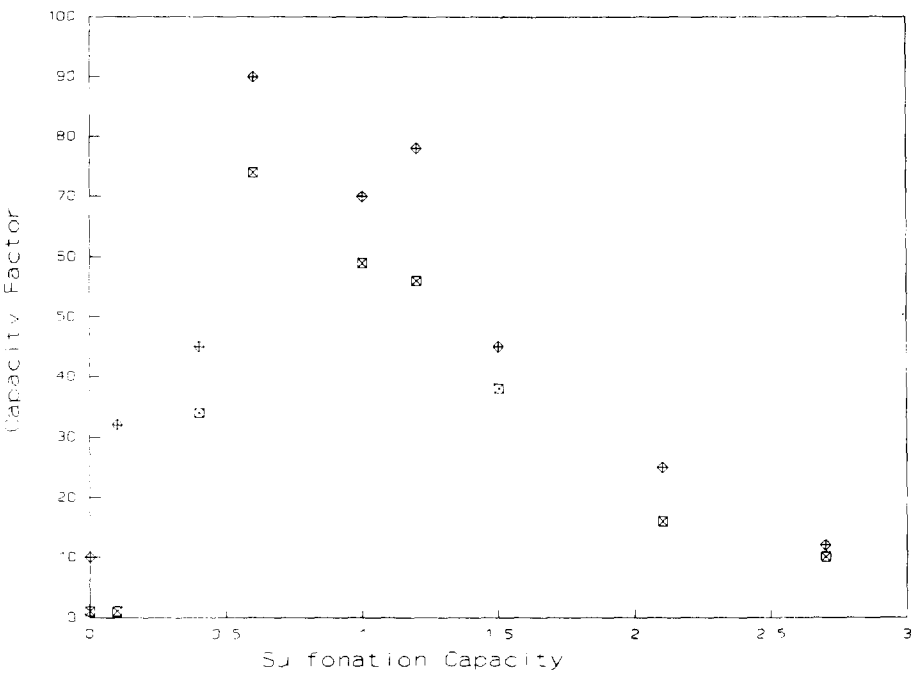

Fig. 2. Effect of PS–DVB sulfonation capacity (in mequiv./g) on retention of catechol in pure water for methanol wetted (◇) and unwetted (□) resins.

Table 3
Comparison between sulfonated (0.4 mequiv./g) and unsulfonated resins

Compound	Recovery (%)			
	Sulfonated		Unsulfonated	
	Not wetted	Wetted	Not wetted	Wetted
Anisole	94	93	83	89
Benzaldehyde	90	89	87	96
Nitrobenzene	96	95	88	96
Hexyl acetate	94	94	84	82
Benzylalcohol	90	98	78	81
Phenol	98	95	77	89
Catechol	59	34	ND	ND
m-Nitrophenol	98	99	89	95
Mesityl oxide	98	97	93	99
tert.-2-Hexenyl acetate	93	90	79	89
Average ± R.S.D. (%)[a]	95 ± 3.2%	94 ± 3.4%	84 ± 5.5%	91 ± 6.3%

Values are averages of three trials. Wetting solvent is methanol. ND = Not detected.
[a] Catechol not included.

tion necessary to produce a hydrophilic resin surface. Underivatized PS–DVB and slightly sulfonated (up to 0.6 mequiv./g) are not wetted by water, while resins with a capacity of 0.6 mequiv./g or greater are wetted.

The lower k' values above 0.6 mequiv./g may be attributed to lower overall hydrophobicity of the resin at higher concentrations of sulfonic acid groups. The hydrophobic resin matrix may become increasingly shielded by the bulky, polar sulfonic acid groups. Wetting with methanol had a greater effect on the lightly sulfonated resins compared to those of higher capacity. The purpose of methanol pretreatment is to increase surface hydrophilicity, but this does not make a large difference with the higher capacity resins. All of the compounds used in this experiment were quite polar, but a similar trend would be expected for more non-polar analytes, although the change may not be as dramatic. Obtaining curves for hydrophobic analytes would be difficult and time consuming. The retention time for phenol, the most non-polar compound used for this study, was about 65 min. Judging by the peak shape, a maximum retention time of about 2 h may still yield a detectable peak, which leads to an upper k' limit for this technique of 1000.

3.3. SPE with sulfonated resins

The ability of sulfonated and unsulfonated resins to extract various organic test compounds from aqueous samples was compared using identical small columns packed with the resins. After the extraction step, the test compounds were eluted with 1.0 ml of ethyl acetate or methanol and determined by GC. The percentage recoveries are given in Table 3. The small resin size (8 μm) allows even the hydrophobic underivatized resin to extract the compounds, but the sulfonated resin, with a more polar surface, is even more efficient for extracting these analytes. Note the sulfonation capacity for this table is 0.4 mequiv./g which is close to the optimum capacity of 0.6 mequiv./g. The effect of wetting the resin with methanol is also shown. As expected, this has a major effect on the underivatized resin, but is not as important with

Table 4
Recoveries of organic solutes (1 ppm) with a sulfonated Empore membrane (0.6 mequiv./g)

Compound	Recovery (%)
Phenol	98
p-Cresol	102
2,5-Dimethylphenol	98
p-Chlorophenol	97
o-Chlorophenol	95
m-Nitrophenol	97
4-*sec.*-butylphenol	98
4-*tert.*-butylphenol	100
4-Hexylresorcinol	101
2-Methylresorcinol	91
p-Isopropylphenol	96
Dodecyl alcohol	94
1-Hexanol	94
Cyclohexanol	93
2-Ethyl-1-hexanol	97
Benzyl alcohol	94
1-Octanol	96
Phenethyl alcohol	96
3-Phenyl-1-propanol	98
Benzonitrile	99
Nitrobenzene	100
3-Nitroacetophenone	98
Benzothiazole	97
o-Nitrotoluene	97
Isophorone	100
Benzophenone	96
Acetophenone	102
Hexyl aldehyde	95
Octyl aldehyde	96
Nonyl aldehyde	93
9-Anthraldehyde	98
Salicylaldehyde	100
Benzaldehyde	104
Anisole	96
Phenetole	91
Ethyl acetoacetate	97
Methyl benzoate	96
Ethyl cinnamate	95
Hexyl acetate	93
tert.-2-Hexenyl acetate	91
Isopentyl benzoate	92
1-Iodoheptane	98
1-Bromododecane	92
1-Chlorododecane	90
Average ± R.S.D. (%)	96 ± 3.1

the sulfonated resin. The surface of the sulfonated resin is hydrophilic enough that methanol does not significantly modify it.

3.4. SPE with resin-loaded membranes

Empore membranes embedded with sulfonated resin of approximately 0.6 mequiv./g were also used for SPE. These membranes embedded with other materials have been used and described previously [11–13]. They offer several advantages over loose resin including lower back pressure necessary to load samples, decreased channeling, and improved mass transfer [14,15]. In this study, sulfonated membranes were used to extract neutral organic compounds from water. Averaged triplicate recoveries of 45 analytes are shown in Table 4. Many classes of compounds are represented including phenols, alcohols, aldehydes, ketones and esters. Polar analytes, like the phenols, and non-polar analytes such as the halogenated alkanes are all efficiently recovered. Recoveries are over 90% for all compounds with relative standard deviations commonly near 3%. These recoveries compare very favorably with data reported previously for alcohol and acetyl derivatized PS–DVB resins and membranes [6,13].

3.5. Analysis of breakthrough curves

The adsorption capacity for several organic compounds was determined by passing a 5- or 10-ppm aqueous solution of the analyte through a resin-loaded membrane until breakthrough occurred. Since breakthrough is closely related to k' [4], the breakthrough volume (V_B) or retention volume (V_R) for a particular analyte is a good indication of the extraction ability of the resin. For this study V_B is defined as the volume after extrapolating the middle portion of the curve to the x-axis, and V_R as the volume at $C/C_0 = 0.5$. C/C_0 is the ratio of analyte effluent concentration to influent concentration. The resin load capacity may also be determined from a breakthrough curve. This is the total number of moles of analyte adsorbed by a resin, and is calculated by multiplying V_R by the influent concentration [16].

Breakthrough curves of several compounds were compared for two Empore membranes —one embedded with underivatized PS–DVB

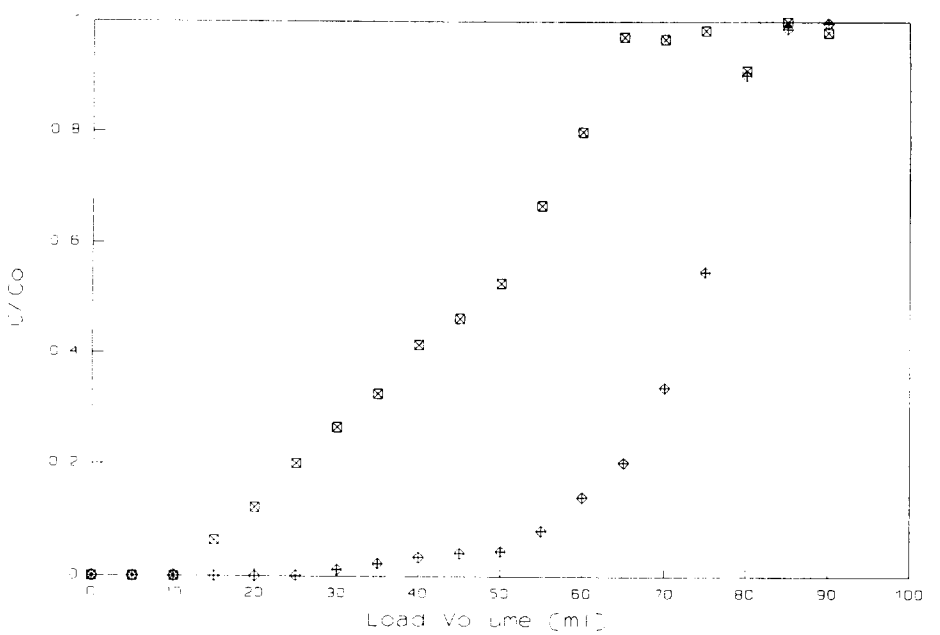

Fig. 3. Breakthrough curves for p-cresol on a sulfonated (◇) and unsulfonated (□) Empore membrane.

Table 5
Comparison of breakthrough data for Empore membranes embedded with unsulfonated PS–DVB and sulfonated (0.6 mequiv./g) PS–DVB

Compound	Load capacity (10^{-6} mol/g)		V_R (ml)		V_B (ml)	
	Sulfonated	Unsulfonated	Sulfonated	Unsulfonated	Sulfonated	Unsulfonated
p-Cresol	74.2	47.4	74	46	34	12
Ethyl acetoacetate	39.3	13.1	46	15	38	0
Nitrobenzene	223	241	126	132	76	28
Isophorone	173	185	109	114	45	27

and the other with sulfonated PS–DVB (0.6 mequiv./g capacity). Breakthrough curves for *p*-cresol are shown in Fig. 3. The sulfonated resin membrane, being more hydrophilic, produces a much sharper breakthrough than the underivatized membrane, which allows breakthrough almost immediately.

The parameters calculated from the breakthrough curves of four compounds are shown in Table 5. Extraction efficiency of the more polar compounds, *p*-cresol and ethyl acetoacetate, is dramatically increased with the sulfonated membrane. Load capacity, V_R, and V_B, are all much larger on this membrane. It may be expected that less polar compounds would be more easily extracted with an underivatized resin, but this is not necessarily the case. The less polar compounds, nitrobenzene and isophorone, do have slightly higher load capacities and V_R on the underivatized membrane, but V_B is still much lower. This is caused by the poor curve shape and early breakthrough on the underivatized membrane. V_B is the parameter of most concern for SPE because dilute samples are usually used and the load capacity of a resin is seldom approached. A sulfonated membrane would therefore be the better adsorbent to use for SPE of these types of compounds.

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