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## PREPARATION AND ION CHROMATOGRAPHIC APPLICATION OF SURFACE-SULPHONATED CATION EXCHANGERS

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### SUMMARY

Low-capacity (0.007–0.500 mequiv./g) surface-sulphonated cation exchangers can be produced from unswollen polystyrene–divinylbenzene copolymers. The optimal sulphonation conditions were determined. The applicability of the resin was demonstrated by the ion chromatographic separation of  $\text{Li}^+$  and  $\text{K}^+$  ions. The homogeneity of the surface of the resin was proved by scanning electron micrographs and by determining the sulphur distribution by X-ray analysis.

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### INTRODUCTION

One of the possible developments in ion-exchange separations would be to make appropriate structural changes to the ion exchanger. If the functional groups are restricted to the surface of the exchanger then the ion diffusion process is significantly reduced and the speed and efficiency of the separation are improved. Horváth and co-workers<sup>1,2</sup> and Kirkland<sup>3</sup> described the first such studies. In these cases the core and the layer carrying the functional groups were chemically different. Skafi and Lieser<sup>4,5</sup> described the possibility of surface sulphonation and found that the new type of resin obtained exhibited favourable kinetic characteristics. Fritz and Story<sup>6</sup> studied the selectivity of such resins. Small *et al.*<sup>7</sup> described a new application of the low-capacity resin, the so-called “ion chromatographic” method.

This paper describes a method for the preparation of a low-capacity surface-sulphonated resin. The effect of sulphonation parameters on the capacity of the resin was studied. The aim of the work was the development of a stable, homogeneous cation exchanger on a styrene–divinylbenzene copolymer matrix.

### EXPERIMENTAL

#### *Materials*

Styrene–divinylbenzene copolymer (with 8% of divinylbenzene) from Dow Chemical (Midland, MI, U.S.A.) was used for the sulphonation experiments. The stripper column was packed with 200–400-mesh Dowex 1-X8 ( $\text{Cl}^-$ ) (Bio-Rad Labs., Richmond, CA, U.S.A.). Reagents were analytical-grade chemicals.

### Procedure

A narrow size fraction (56–74  $\mu\text{m}$ ) of resin was obtained by sieving the 200–400-mesh raw material. The resin was extracted successively with water, ethanol and acetone and dried.

A 5-g amount of styrene–divinylbenzene copolymer without pre-swelling was submerged in 250 ml of thermostated concentrated sulphuric acid. The reaction time and temperature could be controlled and the reaction was carried out in a special reactor. The reactor design ensured that the resin–sulphuric acid mixture could be immediately separated on a vacuum-assisted filter system once the prescribed reaction time was completed. This technique allowed the precise control of the reaction time as the bulk of the reagent could be removed immediately. Traces of acid could remain in the pores which, upon dilution in the aqueous solutions, resulted in the breakage and peeling off of the thin, active shell. Sulphuric acid could be completely removed by washing the resin with moisture-free acetone kept at 30–35°C. Acetone does not swell the resin and undergoes a rapid reaction with sulphuric acid. Sulphonation reactions were carried out at 40, 60, 80 and 90°C for 5–180 min.

The sulphonated resin was washed with ethanol, air-dried and pre-formed in several cycles with 1 *M* sodium chloride solution and 2 *M* hydrochloric acid.

The capacity of the surface-sulphonated ion exchanger was determined by a special coulometric method as described earlier<sup>8</sup>.

A home-made ion chromatographic system was used for the chromatographic experiments (Fig. 1).

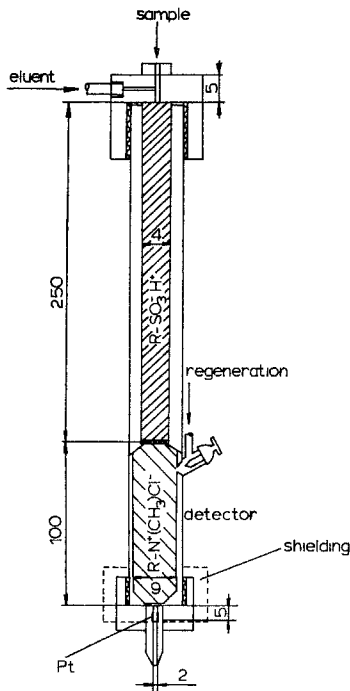


Fig. 1. Ion chromatographic apparatus.

A single-head plunger pump, Type LS-204 (Labor MIM, Budapest, Hungary), a platinum conductivity cell, a Type OK-102 conductometer and a Type OH-814/1 potentiometric recorder (all from Radelkis, Budapest, Hungary) were assembled into an ion chromatograph. Both the separation and stripper columns were packed from an aqueous slurry. Samples were injected with a Hamilton microsyringe.

## RESULTS AND DISCUSSION

The capacity of the resin obtained under different sulphonation conditions (reaction time and temperature) are shown in Fig. 2. It can be seen that low-capacity resins (0.01–0.1 mequiv./g) can be obtained at 80°C with sulphonation times ranging from 30 to 120 min. At 90°C the capacity changes almost linearly with sulphonation time. The capacity of the resin cannot be closely controlled at this temperature. At 40°C and 60°C the length and slope of the middle inflection section are lower. The maximal capacities obtained with a reaction time of 180 min were 0.012 and 0.025, mequiv./g, respectively.

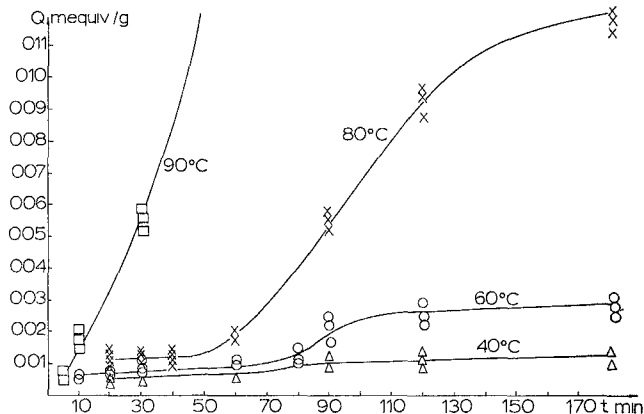


Fig. 2. Effect of sulphonation temperature and time on capacity.

It could be concluded that temperature affected the capacities to a greater extent than reaction time. This indicates that the choice and maintenance of the reaction temperature is of greater importance than those of the reaction time. The results indicate that the optimal reaction temperature range is 60–80°C.

The results shown in Fig. 3 indicate the effect of pre-swelling. The capacity of a resin obtained by sulphonating at 90°C a matrix pre-swollen in methylene chloride as a function of the reaction time is shown by the curve marked 90°C (S). Owing to the more open pore structure caused by the pre-swelling solvent the reaction proceeds within the resin as well, so that truly low-capacity resins cannot be produced.

The regular structure of the surface-sulphonated resins is illustrated in Fig. 4, which shows a scanning electron micrograph of a 0.055-mequiv./g particle (80°C, 90 min). The sulphur distribution across the cross-section of the bead as determined by an X-ray microanalyser is shown in Fig. 5. The two peaks, being proportional in

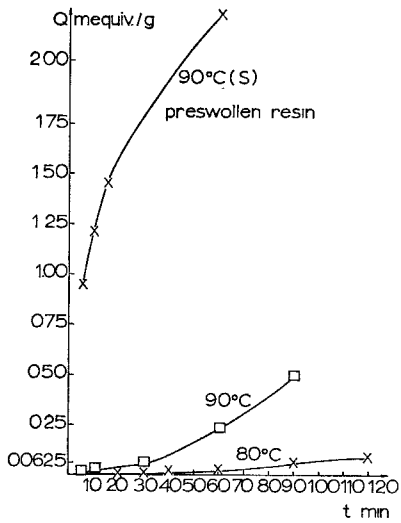


Fig. 3. Effect of sulphonation temperature and time on the capacity. Curve 90°C (S) denotes the capacity changes of the resin pre-swollen in methylene chloride.

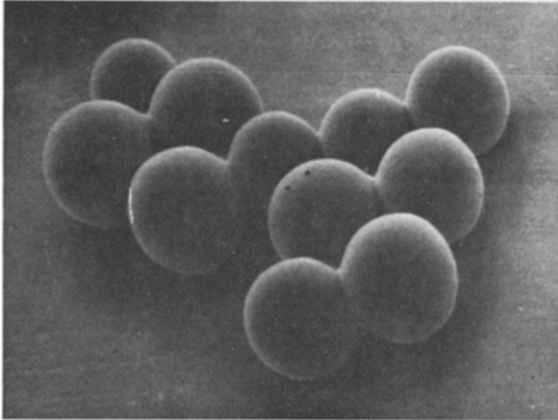


Fig. 4. Scanning electron micrograph (132 $\times$ ) of surface-sulphonated cation exchanger (JEOL 50 A).

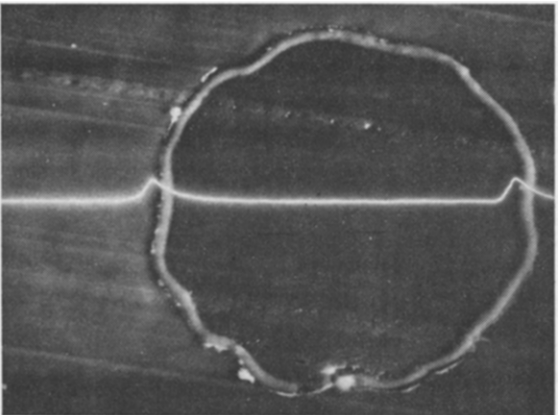


Fig. 5. Secondary electron image (264 $\times$ ) of surface-sulphonated cation exchanger with sulphur (SO<sub>3</sub>H) line scan. X-ray microanalyser system consisting of JEOL 50 A scanning electron microscope and EDAX 707 B analyser. Capacity, 0.055 mequiv./g; sulphonation temperature, 80  $\pm$  0.2°C; sulphonation time, 90 min.

height to the sulphur concentrations, indicate that the  $\text{SO}_3\text{H}$  groups are indeed restricted to the surface of the particle.

The rapid separation of  $\text{Li}^+$  and  $\text{K}^+$  demonstrates the applicability of the resin for ion chromatographic purposes, as shown in Fig. 6.

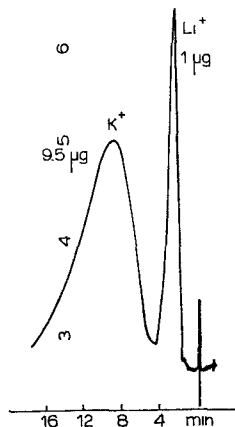


Fig. 6. Rapid separation of  $\text{Li}^+$  and  $\text{K}^+$  ions on a surface-sulphonated cation exchanger (IC system). Eluent, 0.005 M HCl; flow-rate, 2.1 ml/min; sample volume, 2.5  $\mu\text{l}$ ; resin capacity, 0.055 mequiv./g.

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#### REFERENCES

- 1 Cs. Horváth, B. A. Preiss and S. R. Lipsky, *Anal. Chem.*, 39 (1969) 1422.
- 2 Cs. Horváth and S. R. Lipsky, *Anal. Chem.*, 41 (1969) 1227.
- 3 J. J. Kirkland, *J. Chromatogr. Sci.*, 7 (1969) 361.
- 4 M. Skafi and K. H. Lieser, *Z. Anal. Chem.*, 249 (1970) 182.
- 5 M. Skafi and K. H. Lieser, *Z. Anal. Chem.*, 250 (1970) 306.
- 6 J. Fritz and J. N. Story, *J. Chromatogr.*, 90 (1974) 267.
- 7 H. Small, T. S. Stevens and W. Bauman, *Anal. Chem.*, 47 (1975) 1801.
- 8 P. Hajós and J. Inczédy, *J. Chromatogr.*, 201 (1980) 193.