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Note

Preparation of low-capacity anion-exchange resins for ion chromatography on a methacrylic copolymer matrix

ÜLO HALDNA*, REIN PALVADRE, JAAN PENTSHUK and TIA KLEEMEIER
Institute of Chemistry, Academy of Science of the Estonian S.S.R., 200026 Tallinn (U.S.S.R.)
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In recent years, ion chromatography[1] has developed into a convenient, sensitive and efficient method for anion analysis. The method makes use of a separation column containing a pellicular anion-exchange resin of low capacity, typically 0.005–0.1 mequiv./g. This resin is made by chloromethylation and subsequent amination of a macroporous poly(styrene–divinylbenzene) resin, or by coating the surface-sulphonated resin with small (0.1–1 μm) anion-exchange latex particles[2,3].

This paper describes a simple method for the preparation of pellicular low-capacity resin for anion separations by ion chromatography. The aim of the work was the development of a stable anion exchanger on an ethoxymethacrylate–ethylenedimethacrylate copolymer matrix.

EXPERIMENTAL

Materials

The 25–40-μm fraction of Spheron 100 000 ethoxymethacrylate–ethylenedimethacrylate copolymer from Lachema (Brno, Czechoslovakia) was selected because it has large pores (25–50 nm), good mechanical strength and a hydrophilic surface.

The BA-2 water-soluble anion exchanger used (Biokhim-reaktiv, Riga, U.S.S.R.) is a polystyrene containing a number of $-CH_2\overset{+}{N}(CH_3)_3-$ groups. Its solubility in 96% (w/w) ethanol is 9.1% (w/w). The BA-2 anion exchanger was fixed on the Spheron 100 000 surface by a water-insoluble glue. Two kinds of glue were used: cellulose nitrate (collodion cotton) type PSV from Flora (Tallinn, U.S.S.R.), containing 12.0 ± 0.1% (w/w) N and poly(vinyl butyrate) type BF-2 from Sojuzbitkhim (Moscow, U.S.S.R.). The solubility of the cellulose nitrate PSV in acetone–96% (w/w) ethanol (1:24) is 0.65% (w/w). Poly(vinyl butyrate) BF-2 is soluble (5%, w/w) in ethanol.

Procedure

The BA-2 anion exchanger was purchased in the form of a 12% (w/w) aqueous solution. To a 50-ml portion of this solution was added 150 ml of acetone. The BA-2 gel, which is insoluble in this mixture, was filtered, washed with acetone and dried at 40°C under vacuum. The dry anion exchanger was dissolved in 96% (w/w) ethanol to obtain a 1.5% (w/w) solution.

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A 0.30% (w/w) glue solution was made by dissolving the cellulose nitrate in acetone–96% (w/w) ethanol (1:24). With BF-2 glue, the commercial 5% ethanolic solution was diluted with 96% (w/w) ethanol to give the desired 0.30% (w/w) solution of the glue.

To 10 g of Spheron 100 000 (25–40 μm) in a round-bottomed flask were added 20 g of 1.5% (w/w) ethanolic BA-2 anion exchanger solution and 10 g of 0.30% (w/w) glue solution. Ethanol was removed in a rotory evaporator under reduced pressure and at 40°C in the water-bath used to heat the round-bottomed flask. The pellicular anion exchanger was packed into 250 × 3 mm I.D. and 150 × 2 mm I.D. chromatographic columns at a pressure of 70 kg/cm^2.

Eluents

For the system with a suppressor column [200 × 4 mm I.D., filled with KU-2 cation exchanger (Sojuzkhimreaktiv, Moscow, U.S.S.R.)] 0.0015 *M* $NaHCO_3$–0.0012 *M* Na_2CO_3–0.002 *M* NaOH was used as the eluent. For the non-suppressed system, the eluent was 0.0010 *M* benzoic acid.

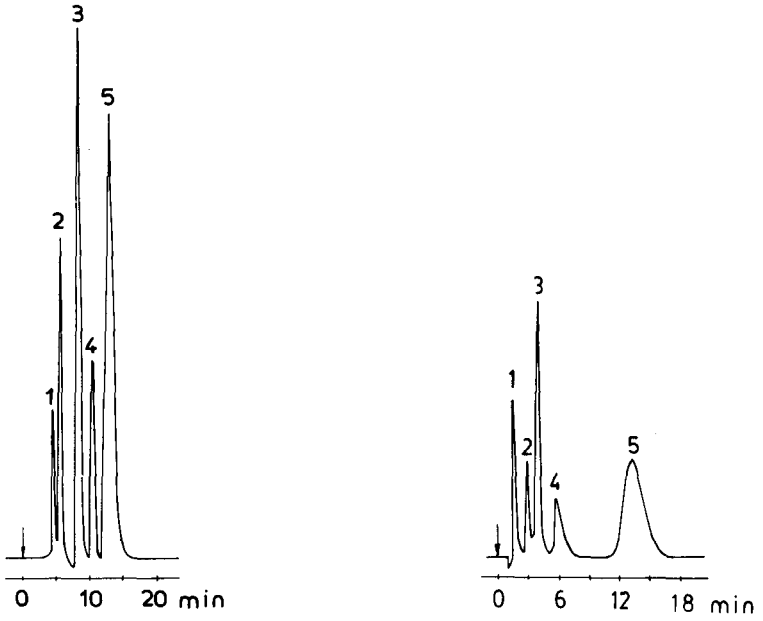

Fig. 1. Chromatogram of 2 ppm of F^- (1), 5 ppm of Cl^- (2), 20 ppm of NO_3^- (3), 25 ppm of PO_4^{3-} (4) and 40 ppm of SO_4^{2-} (5), demonstrating the usefulness of the modified methacrylate resin for the separation of common ions. Experimental conditions: resin made with PSV glue, 25–40 μm fraction; exchange capacity, 0.020 mequiv./cm^3; column, 250 × 3 mm I.D.; eluent, 0.0015 *M* $NaHCO_3$–0.0012 *M* Na_2CO_3–0.0020 *M* NaOH; flow-rate, 1.5 ml/min.

Fig. 2. Chromatogram of 20 ppm of acetic acid (1), 30 ppm of lactic acid (2), 10 ppm of formic acid (3), 30 ppm of valeric acid (4) and 150 ppm of caproic acid (5). Experimental conditions: resin made with BF-2 glue, 25–40 μm fraction; exchange capacity, 0.032 mequiv./cm^3; column, 150 × 2 mm I.D., eluent, 0.0010 *M* benzoic acid; flow-rate, 1.0 ml/min.

Apparatus

An IVK-11 ion chromatograph (TA SKB, Tallinn, U.S.S.R.) equipped with a conductivity detector was used. The volume of the sample loop was 100 μl. The flow-rate was maintained at 1.0 or 1.5 ml/min and the back-pressure was 30–50 kg/cm^2.

RESULTS AND DISCUSSION

Several batches of superficial anion exchanger were prepared by using both kinds of glue (eight batches with PSV and four with BF-2). The capacities of these anion exchangers, determined dynamically with 0.0010 *M* hydrochloric acid, were 0.020 ± 0.003 and 0.035 ± 0.005 mequiv./cm^3 for the resins made with PSV glue and BF-2 glue, respectively.

The resins prepared by the procedures described here exhibit satisfactory chromatographic performance. Figs. 1 and 2 show the chromatograms obtained with these resins.

It can be concluded that the resins prepared are useful for the separation of both inorganic and organic anions. A chromatographic column packed with the resin made with cellulose nitrate has been used for over 5 months with no change in its performance. The exchange capacity of the resin may easily be varied by changing the volumes of solutions added. However, according to our observations, it seems to be necessary to keep the mass ratio of glue to anion exchanger equal to 1:(10 ± 2), otherwise the chromatographic performance on the resin is less satisfactory.

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