SELECTIVE ION EXCHANGERS WITH ISONITROSOACETAMIDE FUNCTIONAL GROUPS. I. SYNTHESIS OF THE ION EXCHANGERS

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The paper describes block polycondensation of *m*-aminophenol with formaldehyde and isonitrosoacetylation of the product. In the same way the isonitrosoacetamide functional group was attached to a styrene–divinylbenzene copolymer after its nitration and reduction.

The selective ion exchangers described herein contain isonitrosoacetamide functional groups (—NH.CO.CH═NOH) attached to the macromolecular skeleton in different ways. The functional group is derived from isonitrosoacetanilide, whose reactivity with metallic ions has been investigated by Zátka[1]. Since 1959 the analytical usability of isonitrosoacetanilide and its derivatives has been studied in detail by Buscaróns and coworkers; they summarized their results some years later[2]. The agent forms insoluble salts with a number of metallic cations. The reaction, strongly dependent on the medium, is most sensitive in the case of palladium in an acid solution (yellow precipitate of $(C_8H_7N_2O_2)_2Pd$). The infrared spectrum suggests a five-membered ring. In these conclusions both authors[1,2] coincide. The preparation of isonitrosoacetanilide is simple and gives high yields. It can be assumed that the synthesis will proceed even with amino groups bound to a macromolecular chain.

Selective ion exchangers with the considered functional groups were prepared in the following ways: the resin obtained by condensation of *m*-aminophenol with formaldehyde was isonitrosoacetylated by reaction with hydroxylammonium chloride and chloral hydrate (type I), isonitrosoacetylation of amino groups on a styrene–divinylbenzene skeleton (type II), condensation of isonitrosoacetanilide with formaldehyde in an acid medium (type III), isonitrosoacetylation of the resin obtained by condensation of aniline with formaldehyde in an acid medium (type IV).

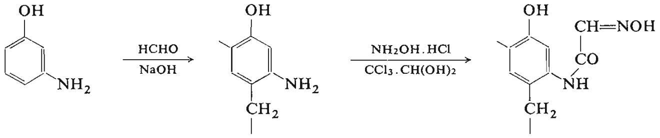
The resins of types III and IV, chemically rather unstable, have been described previously[3]. The syntheses and evaluation of types I and II is the subject of the present paper.

EXPERIMENTAL

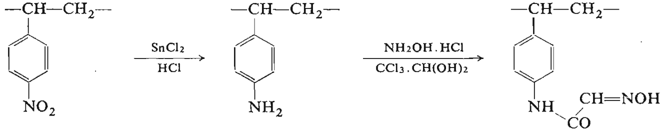
Synthesis of the Selective Ion Exchangers

The steps of the preparation are illustrated in Scheme 1. With either type of ion exchangers the content of water was determined by drying c. 1 g of a moist product at 105°C to a constant weight. We had verified thermogravimetrically that under these conditions no decomposition occurred. The exchange capacities of the two types of exchangers were determined by a batch procedure. One mmol of cations was employed per 0·5 g of the dry weight of the exchanger in a volume of 100 ml in the presence of admixtures adjusting the medium for the sorption. After 24 h the unsorbed portion of the cations was determined in the solution separated from the exchanger under suction. The exchanger was than regenerated by hydrochloric acid.

Type I



Type II



SCHEME 1

Preparation of the type I exchanger: 218·2 g (2 mol) of *m*-aminophenol (purified by repeated crystallization from water in the presence of activated carbon, m.p. 122°C) dissolved in 1 330 ml of 3M-NaOH (4 mol) was condensed with 284 ml (4 mol) of 14·1M-CH_2O (≈ 40% solution.) The temperature rose to 50°C. After 24 h at room temperature the flask with the viscous solution was heated 1 h on water bath; the solution solidified in 15 min. The product (block) was allowed to stand for 24 h at room temperature, then it was crushed, washed with water and allowed to swell. The swollen portion of particle size 0·30 to 0·60 mm was sorted out and collected on a filter; yield 1 140 g of the wet product (dry weight 15·5%). For the elementary unit of the polycondensate C_7H_7NO (121·1) calculated: 11·55% N; found: 9·41% N.

To 390 g of the wet polycondensate (dry weight 60·5 g, 0·5 mol) was added a solution of 52·1 g of $NH_2OH.HCl$ (0·75 mol) in 600 ml of water and a solution of 89·4 g of chloral hydrate (0·54 mol) in 600 ml of water, both solutions being pre-heated to 70°C. In the course of 25 min the reaction mixture was brought to boil under constant stirring and kept boiling for 10 min. After 24 hours' standing at room temperature the ion exchanger was poured into a column and thoroughly washed with water; its exchange capacity, determined with an aliquot sample, was 1·38 mmol Cu^{2+} per gram of the dry product. The dry weight of the ion exchanger was 43·9%. For the elementary unit $C_9H_8N_2O_3$ (192·2) calculated: 14·58% N; found: 11·70% N.

Preparation of the type II exchanger: 208 g of a styrene–divinylbenzene copolymer swollen in chloroform (2% of DVB, dry weight 50 g) was nitrated according to Davies and coworkers[4]. For $C_8H_7NO_2$ (149·1) calculated: 9·32% N; found: 9·02% N. The compound was reduced according to the same authors[4]; for C_8H_9N (119·2) calculated: 11·75% N, found: 11·88% N.

206 g of the wet aminopolystyrene (2% of DVB, dry weight 47·7 g, 0·4 mol) was mixed with hot solutions of 41·7 g of $NH_2OH.HCl$ (0·6 mol) in 600 ml of H_2O and 71·5 g of chloral hydrate (0·432 mol) in 600 ml of H_2O. Under constant stirring the mixture was brought to boil and kept boiling for 1 h. On mixing the components the solution had had pH 3, during the boiling the acidity increased. After standing for 15 h at room temperature the ion exchanger was washed by decantation of water and collected on a filter. The dry weight of the product was 44·7%, its exchange capacity was 1,23 mmol Cu^{2+} per gram of the dry substance. For $C_{10}H_{10}N_2O_2$ (190·2) calculated: 14·75% N; found: 11·57% N.

RESULTS

The experiments have shown that *m*-aminophenol in an alkaline medium readily undergoes condensation with formaldehyde to a resin which is a good starting substance for further syntheses. The methylene interlinks are attached to the benzene rings at *o*- and *p*- positions to the phenolic hydroxyl and the amino groups remain free. The block polymerization is independent of the molar ratios of the starting components in a rather wide range.

The isonitrosoacetylation of the amino groups on the macromolecular skeleton by the mixture of hydroxylammonium and chloral hydrate in an acid medium was conducted under the conditions employed in the Sandmeyer synthesis of isonitrosoacetanilide modified by Marvel and Hiers[5]. The reaction was tested on the polycondensate prepared as described above; its extent was evaluated by determining the exchange capacity for Cu^{2+} ions in an acetate buffer, pH 5. It has been found that the acidity of the mixture is sufficient for the synthesis even without an addition of HCl, which reduced the swelling of the polycondensate. Likewise and probably for the same reason, the capacity of the product was reduced by an addition of sodium sulphate, necessary for the preparation of isonitrosoacetanilide. The effects of temperature and heating time of the reaction mixture have been investigated in more detail. No appreciable differences in exchange capacity were found in a temperature range 70–100°C and within the range of heating time from 5 seconds to 7 hours (1·32 to 1·46 mmol Cu^{2+} per g of the dry exchanger). Further we observed that isonitrosoacetylation of the resin does not require so great an excess of hydroxylammonium as the cited authors state[5]. The exchange capacity of the ion exchanger decreased by only 11% if an equimolar ratio of hydroxylammonium chloride to amine groups was employed. Therefore we employed an excess of 1·5 mol of hydroxylammonium chloride per mol of amino groups, and the capacity of the exchanger was only 7% lower than at a molar ratio of 3·6.

In the repeated determination of exchange capacity there was observed a decrease by as much as 11·5%, mainly in the first three working cycles, which is normal with new exchangers. For further tests of the exchanger it was necessary to bring its capacity to a final level, common for the whole batch. We have therefore studied various ways of recycling a new exchanger. The best procedure has proved to be alternate recycling on a column with a mixture of 1M-CH_3COONa and 0·1M-$K_2S_2O_8$, then with 1M-HCl, always with a passage of water in between. The exchange capacity dropped by 1·4% after the first cycle an no longer decreased. The choice of the solutions for the recycling was motivated by our attempt to suppress the red-ox interaction of the resin and Cu^{2+} ions, since in repeated determination of the capacity for Zn^{2+} ions no appreciable decrease in capacity occurred. The reducing effects of similar resins had been observed by us previously[6,7].

In the synthesis of an exchanger of type II we started from a little cross-linked styrene-divinylbenzene copolymer (2% of DVB) with a macroporous structure (product of the Research Institute of Synthetic Resins and Paints, Pardubice), in which rather bulky functional groups can be built up. The treatment of the copolymer consisted in sorting out the particle size 0·1 to 0·6 mm and 24 hours' extraction in chloroform. The chloroform was then filtered off and the dry weight of the copolymer was determined (24%). To obtain a chemically resistant and selective ion exchanger the copolymer was nitrated, the nitro groups reduced to amino groups and the amino groups were isonitrosoacetylated.

In the isonitrosoacetylation we made use of the findings obtained with the type I exchanger. The only difference was that in the case of type II it was better to keep the reaction mixture boiling for a longer time (1 h). The capacity of this ion exchanger also exhibited a moderate decrease in the first three cycles; the total decrease was 7·8%. It has been ascertained that recycling with solution of $CH_3COONa + K_2S_2O_8$ and HCl has the same levelling effect on the capacity as with type I. The synthesis of ion exchangers with isonitrosoacetamide functional groups has been patented[8]. The properties and utilization of these ion exchangers are subject of our further study[9].

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