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## PREPARATION AND PROPERTIES OF A STYRENE-ETHYLENE DIMETHACRYLATE COPOLYMER-BASED CHELATING ION EXCHANGER WITH BONDED 8-HYDROXYQUINOLINE

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An optimum procedure was sought for the fixation of 8-hydroxyquinoline to styrene-ethylene dimethacrylate copolymer (SE-gel) with respect to the capacity of the resulting ion exchanger. The time of establishment of the sorption equilibrium, pH-dependence of the distribution coefficient of  $\text{Cu}^{2+}$  ions, sorption isotherm of  $\text{Cu}^{2+}$  ions, and the ion exchanger stability were determined.

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Owing to their selectivity, chelating ion exchangers find ever-increasing use for the sorption of heavy metals; they are employed most frequently for the separation of trace concentrations of heavy metals from salt solutions and for the preconcentration of metal ions from highly dilute solutions<sup>1</sup>. A prerequisite for this, in addition to selectivity, is a rapid establishment of the sorption equilibrium. The highest possible capacity and a good stability are also desirable for the application of chelating ion exchangers in the industrial practice to the reclamation of metals, purification of waste waters or solutions, *etc.* A reasonable time of establishment of the sorption equilibrium is here also necessary. For these reasons, nonselective ion exchangers are actually often preferred in the industrial practice.

Of the hitherto studied chelating ion exchangers, high capacities ( $>1 \text{ mmol g}^{-1}$ ) have been found for those prepared by polymerization or polycondensation and for polystyrene-based ion exchangers<sup>2</sup>. Polymeric preparation of high-quality chelating ion exchangers is very difficult<sup>2</sup>. Polystyrene-based ion exchangers exhibit poor kinetic properties because of the hydrophobic nature of the matrix<sup>3</sup> (it takes hours for the equilibrium to establish). A considerably more hydrophilic matrix, *viz.* a styrene-ethylene dimethacrylate 1 : 1 copolymer (SE-gel) was obtained by substituting the crosslinking agent (divinylbenzene) by ethylene dimethacrylate; this hydrophilic nature and the styrene basis of the matrix are factors owing to which both a faster establishment of the sorption equilibrium and a high capacity could be expected.

In the present work, a procedure suitable for the fixation of 8-hydroxyquinoline, as a group-selective reagent suitable for industrial application, to the styrene-

ethylene dimethacrylate copolymer was sought with a view to attaining the maximum sorption capacity, and the properties of the ion exchanger obtained were studied.

### EXPERIMENTAL

The styrene-ethylene dimethacrylate copolymer (SE-gel) was commercial Separon SE (Laboratorní přístroje, Prague); fraction of 75–125  $\mu\text{m}$  particle size and  $70 \text{ m}^2 \text{ g}^{-1}$  specific surface area was used. One g of SE-gel was added to nitration mixture at  $0^\circ\text{C}$ , and in 1 h, the temperature was raised to a prerequisite value (Table I) and held so for 3 h. Then the reaction mixture was poured onto 100 ml of ice/water and the modified gel was washed to a neutral reaction and dried at  $100^\circ\text{C}$ .

The nitrated SE-gel was reduced by procedures described for nitropolystyrene<sup>4,5</sup> and for *p*-nitrobenzoyl chloride-modified silica gel<sup>6</sup>. To the reductant (Table II) was added 0.25 g of the nitrated SE-gel and the mixture was heated at  $90^\circ\text{C}$  for 20 h. The gel then was filtered out, washed in turn with distilled water, 12 ml of 2M-NaOH and 10 ml of 5M-HCl, and used immediately for diazotization and coupling to 8-hydroxyquinoline by the procedure used before for glycidyl methacrylate gel<sup>7</sup>.

The analytical properties of the resulting chelating ion exchanger were tested *via* sorption of  $\text{Cu}^{2+}$  ions<sup>8</sup>. Each sample was twice suspended shortly in 5M-HCl (25 ml per 0.5 g of exchanger) before use. The sorption ability was expressed in terms of the statically determined practical sorption capacity. The time of establishment of the sorption equilibrium, pH-dependence of the distribution coefficient of  $\text{Cu}^{2+}$  ions, sorption isotherm of  $\text{Cu}^{2+}$  ions, and stability of the chelating ion exchanger were also determined.

### RESULTS AND DISCUSSION

For the fixation of 8-hydroxyquinoline to SE-gel, use was made of experience gained from the preparation of the polystyrene-divinylbenzene copolymer-based ion ex-

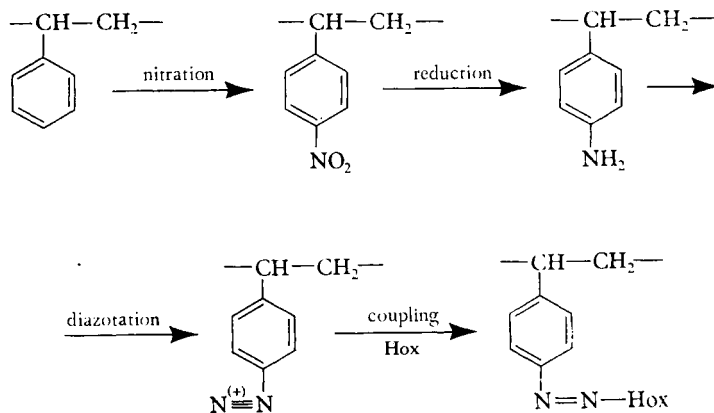
TABLE I

Nitration of SE-gel (1 g) with a mixture of concentrated nitric acid (10 ml) and concentrated sulphuric acid (20 ml)

$t$ $^\circ\text{C}$	Time h	Product weight g	$[-\text{NO}_2]_{\text{gel}}$ $\text{mmol g}^{-1}$	$Q_a(\text{Cu}^{2+})$ $\text{mmol g}^{-1}$
15 <sup>a</sup>	3	1.10	3.68	—
25	3	1.18	4.82	0.97
50	3	—	6.25	1.40
55	3	1.32	6.60	—
55 <sup>b</sup>	3	1.02	1.95	—
55	8	—	6.74	0.22
70	3	—	6.88	0.20

<sup>a</sup> Nitration in 50 ml of acetanhydride; <sup>b</sup> nitration in 50 ml of glacial acetic acid.

changers. The first step of the synthesis is nitration of the gel, *i.e.*, introduction of a nitro group into the benzene ring of the 1-phenylethylene constitutional unit of the copolymer; the next steps are reduction of the nitro group, diazotization of the amino group formed and coupling to 8-hydroxyquinoline.



For the two first steps, the optimum conditions with respect to the capacity of the resulting ion exchanger were sought. Of several classical nitration procedures, the best results were obtained by using a mixture of concentrated nitric and sulphuric

TABLE II

Reduction of 0.25 g of nitrated SE-gel (50.2% C, 4.20% H, 9.24% N;  $[-\text{NO}_2] = 6.6 \text{ mmol g}^{-1}$ ) at 90°C for 20 h

Reductant	Medium	Solvent	Yield %	% C	% H	% N	% O
SnCl <sub>2</sub> (4 g)	conc. HCl (4.5 ml)	ethanol (5 ml)	66	60.5	7.28	9.30	22.9
Sn (1.5 g)	conc. HCl (10 ml)	ethanol (10 ml)	75	61.9	7.64	9.52	20.9
Sn (1.5 g)	conc. HCl (5 ml)	water (5 ml)	51	58.4	7.23	8.96	25.4
Sodium dithionite (1.5 g)	0.1M-NaOH (10 ml)	water (20 ml)	—	39.3	4.64	6.25	49.8

acids. The nitration yield could be increased neither by raising the nitration temperature (50–70°C) nor by extending the reaction time (Table I); moreover, under these conditions the matrix structure changed (voluminous particle aggregations resulted). A partial hydrolysis of ethylene dimethacrylate took probably place during the reaction under the extreme conditions as indicated by the slight weight loss after extraction with benzene and by the extract evaporation residue. Chelating ion exchangers prepared from such nitrated SE-gels exhibited poor capacities. The results show that for the benefit of the practical sorption capacity, SE-gel should be never nitrated to the maximum extent. It was found by calculation that in a gel whose nitro group content is  $6.67 \text{ mmol g}^{-1}$  there are approximately 2.1 nitro groups per benzene ring. The bulky nitro groups in the ortho position with respect to the alkyl chain are sterically shielded; as a consequence, the yield of the ensuing reaction steps is lowered and the diffusion of the metal ions to the functional groups is hindered and these often cannot assume an arrangement suitable for chelation. The experimentally established optimum nitro group content was  $6.25 \text{ mmol per g}$  of dry nitrated SE-gel, hence, in average, 1.9 nitro groups per benzene ring.

In comparison to the polystyrene–divinylbenzene copolymer<sup>4</sup>, more than twice as many nitro groups can be bonded to the benzene rings of SE-gel under identical conditions. The reactivity of SE-gel is increased by the hydrophilization of the matrix by ethylene dimethacrylate. The gel swells sufficiently in the inorganic acids, so that, in contrast to the polystyrene–divinylbenzene copolymer<sup>4</sup>, it need not be previously swelled in an organic solvent.

The degrees of conversion in the reduction steps were calculated by comparing the elemental composition of the aminated SE-gels with that of the starting nitrated SE-gel. The best results were achieved on reduction with tin in a concentrated hydrochloric acid–ethanol 1 : 1 mixture (ethanol ensures a sufficient swelling of the nitrated gel and facilitates the electron transfer). Diazometric titration of the amino groups in the reduced gel afforded incorrect values because of their slow diazotization. The hydrophilic nature of SE-gel played a positive role also in the reduction step (the reduction yields for the polystyrene–divinylbenzene copolymer were as low as<sup>4,5</sup> 50–60%).

The diazotization of the aminated SE-gel and coupling to 8-hydroxyquinoline proceeds with lower yields than the preceding steps (50% together), which is apparently due to the higher steric demands of the coupling reaction.

The optimum nitration and reduction procedure was employed for a reproducible preparation of a chelating ion exchanger exhibiting a high practical sorption capacity; the value determined by static sorption of  $\text{Cu}^{2+}$  ions was  $1.45 \pm 0.05 \text{ mmol g}^{-1}$ .

The time of establishment of the sorption equilibrium agrees with the medium hydrophilic nature of the matrix and the good accessibility to the majority of the functional analytical groups (Fig. 1) (of those suiting to chelation). The equilibrium establishes particularly rapidly at low degrees of saturation: for a 10% capacity

saturation the sorption was 95% in 5 min. Both a fast establishment of equilibrium and a high sorption capacity are important for practical applications of the exchanger. In order to express them both at a time, we suggest a quantity referred to as "one-minute capacity" ( $Q_a^{\text{minute}}$ ), which is the amount of metal sorbed on a gramme of exchanger in a minute from a solution whose concentration corresponds to the saturation of the exchanger. For the SE-gel-based chelating ion exchanger under study, the one-minute capacity was rather high,  $Q_a^{\text{minute}}(\text{Cu}^{2+}) = 0.30 \text{ mmol g}^{-1}$ .

Similarly as other ion exchangers with fixed 8-hydroxyquinoline<sup>8,9</sup>, the ion exchanger prepared exhibits, at low degrees of saturation, high distribution coefficient values for  $\text{Cu}^{2+}$  ions even at low pH (Fig. 2). The slope of the linear segment of the pK-dependence is 1.8, which indicates that in addition to  $\text{ML}_2$  type complexes, ML complexes are also formed even at low degrees of saturation.

The suitable sorption properties are also documented by the wide linear span of the sorption isotherm (about 75% capacity). Approximately 1.1 mmol  $\text{Cu}^{2+}$  ions can be sorbed on a gramme of exchanger without reducing appreciably its sorption ability (Fig. 3). Saturation of the ion exchanger takes place at a relatively small excess of  $\text{Cu}^{2+}$  ions.

The chemical stability of the exchanger is good, as evidenced by the static sorption capacity measured in sorption-desorption cycling experiments. The initial static sorption capacity,  $1.44 \text{ mmol g}^{-1}$ , changed after the 5th, 10th, 15th, and 20th cycle to 1.41, 1.41, 1.48, and  $1.45 \text{ mmol g}^{-1}$ , respectively. Hydrolytic decomposition induced by a long-term action of dilute hydrochloric acid appeared only in 48 h,

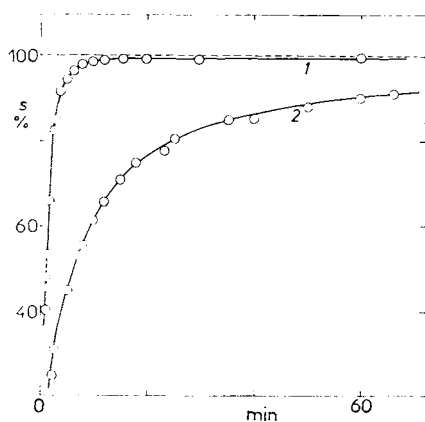


FIG. 1

Time of establishment of sorption equilibrium of  $\text{Cu}^{2+}$  ions ( $s$ ) on SE-gel-based ion exchanger. 1 10% saturation, 2 complete saturation

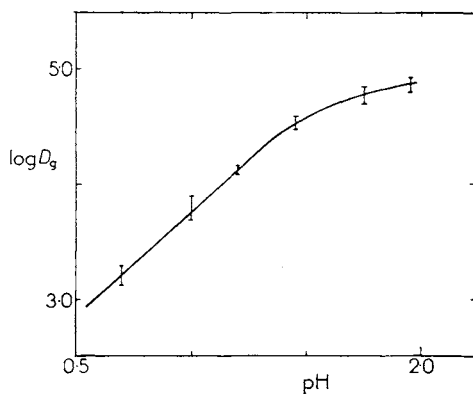


FIG. 2

pH-dependence of distribution coefficient of  $\text{Cu}^{2+}$  ions on SE-gel-based ion exchanger

when the sorption capacity decreased by 9% and 15% in the presence of 3M and 5M-HCl, respectively. In comparison with the similar polystyrene-divinylbenzene-copolymer-based ion exchanger, the stability of the material under study is somewhat lower due to the presence of ester bonds in the matrix skeleton.

TABLE III

Properties of ion exchangers with bonded 8-hydroxyquinoline. Time of equilibrium establishment,  $t_{100}$ , at low degrees of exchanger saturation (up to 15%). Sorption capacity,  $Q_a(\text{Cu}^{2+})$  determined at pH 4–5

Matrix	Link	$t_{1/2}$ min	$t_{100}$ min	$Q_a(\text{Cu}^{2+})$ mmol g <sup>-1</sup>	Hydrolytic stability	Ref.
Silica gel	—NH—CO—C <sub>6</sub> H <sub>4</sub> — —N=N—	—	2	0.07	pH 0–9	6
2-Hydroxyethyl methacrylate	—(CH <sub>2</sub> ) <sub>2</sub> —SO <sub>2</sub> —C <sub>6</sub> H <sub>4</sub> — —N=N—	—	5	0.25	2M-HCl—2M-NaOH	9
Cellulose	—(CH <sub>2</sub> ) <sub>2</sub> —SO <sub>2</sub> —C <sub>6</sub> H <sub>4</sub> — —N=N—	—	<5	0.60	pH 0–13	10
Polystyrene	—N=N—	<60	—	0.48	5M-HCl—5M-NaOH	11
Polystyrene	—NH—C(:S)—NH—	45	—	0.90	pH 1–14	12
Polystyrene	—CH <sub>2</sub> —	55	—	0.42	5M-HCl—5M-NaOH	12
SH-40	—NH—C <sub>6</sub> H <sub>4</sub> —N=N—	0.5	5	0.24	2M-HCl	13
G-gel	—O—C <sub>6</sub> H <sub>4</sub> —N=N—	0.8	9	0.20	—	7
SE-gel	—N=N—	5.2	15	1.40	3M-HCl	this work

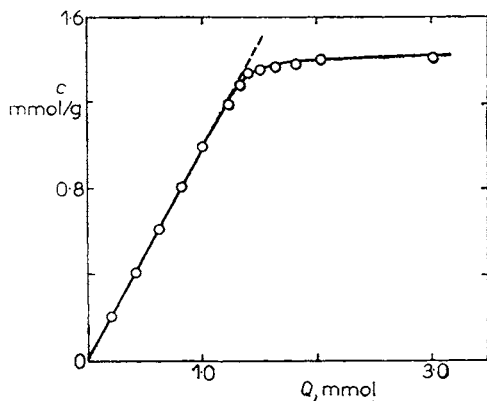


FIG. 3  
Sorption isotherm of  $\text{Cu}^{2+}$  ions at pH 4.6 on SE-gel-based ion exchanger;  $c$  is the  $\text{Cu}^{2+}$  ion concentration in the exchanger phase,  $Q$  is the amount of  $\text{Cu}^{2+}$  ions in solution

On the whole, the SE-gel-based material appears to be a good ion exchanger (Table III). It exhibits the highest sorption capacity of all the hitherto obtained ion exchangers prepared by fixation of 8-hydroxyquinoline to a polymeric matrix. Although the hydrophobic polystyrene is a major constituent of the matrix, the establishment of the sorption equilibrium proceeds one order of magnitude faster than with the polystyrene-divinylbenzene copolymer-based exchanger, owing to the hydrophilization of the gel by ethylene dimethacrylate. The sorption rate is even comparable to that of some ion exchangers on the basis of typically hydrophilic matrices such as cellulose, glycidyl methacrylate gel, *etc.* These properties, along with the wide linear span of the sorption isotherm, high distribution coefficients at low degrees of saturation, and very good hydrolytic stability, render the ion exchanger suitable for practical applications, particularly for extractions of heavy metals.

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