

PREPARATION AND PROPERTIES OF EPOXIDED SEPARON-BASED ION EXCHANGERS WITH BONDED 8-HYDROXYQUINOLINE

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The direct fixation of copper(II) 5-(4-hydroxyphenylazo)-8-quinolinate and the indirect fixation of 8-hydroxyquinoline to Separon H 40 E_{\max} and Separon H 1000 E_{\max} were compared from the point of view of the practical sorption capacities of the resulting ion exchangers. For the ion exchanger obtained by indirect fixation of the reagent to Separon H 40 E_{\max} , the rate of establishment of the sorption equilibrium, pH-dependence of the distribution coefficient of Cu^{2+} ions, and the stability were determined and compared with those of a G-gel-based ion exchanger.

Hydrophilic macroporous polyacrylate gels proved to suit well for the fixation of analytical reagents. Slovák and coworkers used a 2-hydroxyethyl methacrylate-ethylene dimethacrylate copolymer for the preparation of chelating ion exchangers with bonded 8-hydroxyquinoline¹, salicylic acid², and thiol groups³. The materials obtained exhibited very good kinetic properties and chemical stability and a selectivity corresponding to the functional analytical groups fixed. Their low sorption capacity was a shortcoming.

From the synthesis point of view, polyacrylate gels containing the reactive epoxy groups appear to be suitable matrices for the fixation of analytical reagents⁴, and a general synthesis procedure has been worked out for the fixation.⁵ Direct fixation of a modified copper(II) complex of the reagent in pyridine proved to be a convenient method for macroporous gels with pore size larger than approximately 100 nm. Another method of reagent immobilization is the indirect fixation to a gel modified by 1,4-diaminobenzene, which is sterically less demanding and thus is suitable particularly for gels with smaller pore size. These approaches were applied to the fixation of 8-hydroxyquinoline to a glycidyl methacrylate-ethylene dimethacrylate copolymer (G-gel); the chelating ion exchanger obtained displayed good kinetic properties and selectivity, its capacity, however, was rather low and stability was poor due to the residual activity of the glycidyl methacrylate gel⁶.

More favourable properties, particularly from the stability point of view, can be expected for ion exchangers based on Separon H 40 E_{\max} or H 1000 E_{\max} , epoxidized 2-hydroxyethyl methacrylate-ethylene dimethacrylate copolymers (21 and 76% wt.

of the former component, respectively) where the epoxy groups are located predominantly on the particle surface.

The aim of the present work was to immobilize 8-hydroxyquinoline on the two Separons, study the properties of the resulting ion exchangers and compare them with those of the G-gel-based ion exchangers.

EXPERIMENTAL

Separon H 40 E_{\max} (particle size 50–90 μm , specific surface area 230–330 $\text{m}^2 \text{g}^{-1}$, epoxy group content 1.0–1.1 mmol g^{-1} , mean pore diameter 37 nm, pore volume 1.69 ml g^{-1}) and H 1000 E_{\max} (particle size 50–90 μm , specific surface area 20–60 $\text{m}^2 \text{g}^{-1}$, epoxy group content 1.7 mmol g^{-1}) were used. 8-Hydroxyquinoline was fixed to them by procedures that had proved suitable for G-gel, *viz.* direct fixation of copper(II) 5-(4-hydroxyphenylazo)-8-quinolate in pyridine or in dimethylformamide (catalyzed by sodium amide), and indirect fixation of the reagent involving immobilization of 1,4-diaminobenzene in the first step. The ion exchanger samples obtained were suspended shortly in 1 M-HCl prior to testing.

The properties of the chelating ion exchangers were investigated *via* sorption of Cu^{2+} ions which were eluted from the samples with 10 ml of 2M-HCl. Each determination was performed in triplicate at least, and the average values are tabulated.

The theoretical and practical sorption capacities were determined for each ion exchanger sample. For the indirect fixation of 8-hydroxyquinoline, the apparent theoretical capacity (Q'_g) calculated from the analysis of the sample for nitrogen disagrees with the true theoretical capacity; this lies between Q_g^C and Q_g^D , values corresponding to the theoretical capacity provided that all nitrogen increasing the true theoretical capacity from Q_g to Q'_g is associated with the unreacted amino derivative of the starting gel (Q_g^C) or, at a 100% diazotization, with the diazonium salt decomposition product (Q_g^D). The two capacities are calculated as

$$Q_g^C = (2Q'_g - [-\text{NH}_2]) / (1 - 0.156[-\text{NH}_2])$$

$$Q_g^D = (4Q'_g - [-\text{NH}_2]) / (3 - 0.156[-\text{NH}_2])$$

Additional properties, *viz.* the rate of establishment of the sorption equilibrium, pH-dependence of the distribution coefficient of Cu^{2+} ions, sorption isotherm of Cu^{2+} ions, and stability⁶, were only measured for the ion exchanger prepared by indirect fixation of 8-hydroxyquinoline to Separon H 40 E_{\max} .

RESULTS AND DISCUSSION

The smaller mean pore size of the Separons as compared to G-gel manifested itself appreciably in the fixed reagent content of the ion exchangers prepared by the different procedures (Table I). The highest practical sorption capacity was observed for the Separon H 40 E_{\max} based ion exchanger prepared by the indirect fixation. The higher steric demands of the direct fixation brought about a lower reagent content in the corresponding ion exchanger. Being located predominantly on the surface, the epoxy groups of Separon H 40 E_{\max} react with the small molecules of the fixation intermediate (1,4-diaminobenzene) in the indirect fixation more

readily than with the bulky molecules of the modified reagent. The easy accessibility of the reactive groups of the modified gel was responsible for the higher degrees of conversion in the individual steps of the indirect fixation procedure as compared to G-gel (Table II).

TABLE I

Sorption capacities of the Separon-based chelating ion exchangers with bonded 8-hydroxyquinoline

Separon type	Synthesis	$[-NH_2]^a$ mmol g ⁻¹	$Q_a(Cu^{2+})$ mmol g ⁻¹	$Q_g(N)$ mmol g ⁻¹
H 40 E _{max}	direct ^b	—	0.16	0.36
H 40 E _{max}	direct ^c	—	0.13	0.30
H 40 E _{max}	indirect ^d	0.61	0.25	0.51 ^e
H 40 E _{max}	indirect ^f	0.50	0.22	0.44 ^e
H 1000 E _{max}	direct ^b	—	0.12	0.50
H 1000 E _{max}	direct ^c	—	0.07	0.12
H 1000 E _{max}	indirect ^d	0.86	0.11	0.73 ^e

^a Calculated from analysis for nitrogen; ^b in pyridine, without catalyst; ^c in dimethylformamide, catalyzed by NaNH₂; ^d catalyzed by 4-nitrophenol; ^e theoretical capacity calculated from total nitrogen, including unreacted retained intermediates; ^f without catalyst.

TABLE II

Conversions of the reactions in the indirect fixation of 8-hydroxyquinoline to Separon H 40 E_{max}, Separon H 1000 E_{max} and G-gel, respectively, and capacities of the ion exchangers obtained; $[-O-]$ epoxy group content, $[-NH_2]$ amino group content, $Q'_g(N)$ apparent theoretical sorption capacity, Q_g^C theoretical sorption capacity at a 100% coupling, Q_g^D theoretical sorption capacity at a 100% diazotization, $Q_a^{dyn}(Cu^{2+})$ practical sorption capacity determined dynamically, $Q_a^{st}(Cu^{2+})$ practical sorption capacity determined statically, (all in mmol g⁻¹); ξ_A degree of amination conversion, ξ_C degree of diazotization and coupling conversion together calculated from Q_C , ξ_D degree of diazotization and coupling conversion together calculated from Q_D (the true value lies between ξ_C and ξ_D) (all in %)

Matrix	$[-O-]$	$[-NH_2]$	$Q'_g(N)$	Q_g^C	Q_g^D	Q_a^{dyn}	Q_a^{st}	ξ_A	ξ_B	ξ_C
SH 40	1.1	0.57	0.48	0.46	0.46	0.24	0.24	55	82	90
SH 1000	1.7	0.86	0.69	0.61	0.67	0.10	0.18	55	76	87
G-gel	3.5	1.50	1.02	0.70	0.93	0.19	0.20	51	51	75

The high reactivity of the diazotized fixed intermediate is also indicated by the high yield of the coupling to the reagent (about 75%) whose reaction time was shortened to approximately a tenth, *i.e.*, to 20 min. Although the theoretical capacity of the chelating ion exchanger obtained was 25% lower than that of the exchanger prepared by the standard procedure, its practical sorption capacity was only 7% lower.

The experiments confirmed both the positive effect of the catalysis by 4-nitrophenol on the fixation of 1,4-diaminobenzene and the negative effect of a mixed solvent on this reaction. The diazotization of the modified gel was performed in 1M to 5M-HCl. The theoretical or the practical sorption capacities of the ion exchangers prepared from the corresponding intermediate products did not differ appreciably; the highest values were obtained in 5M-HCl (Table III). In more dilute acid, the decomposition of the diazonium salt probably played a part.

Separon H 1000 E_{\max} did not appear suitable as a matrix for chelating ion exchangers (Table I). Although the starting gel contained more epoxy groups, the ion exchangers displayed low sorption capacities, independently of the synthesis procedure. The rather high theoretical capacities as well as the high difference between the dynamically and statically determined practical sorption capacities indicate poor kinetic properties of the exchangers. Because of the smaller specific surface area of Separon H 1000 E_{\max} as compared with Separon H 40 E_{\max} , the epoxy groups occur not only on the surface but also in deeper layers. The arrangement of the functional analytical groups inside the ion exchanger particles then is not very favourable for chelation or the groups are difficult to access by hydrated metal cations; this fact was also responsible for the poorer degrees of diazotization and coupling conversion (Table II).

Because of the low capacity and presumed poorer kinetic properties of the exchanger based on Separon H 1000 E_{\max} , the other properties were only examined

TABLE III

Effect of concentration of hydrochloric acid (c , in mol l^{-1}) used during the diazotization of 4-aminophenylated Separon H 40 E_{\max} on the capacities of the resulting ion exchangers (in mmol g^{-1}); $[-\text{NH}_2] = 0.52 \text{ mmol g}^{-1}$. For symbols see Table II

c	$Q'_g(\text{N})$	$Q_g^C(\text{N})$	$Q_g^D(\text{N})$	$Q_d(\text{Cu}^{2+})$
1	0.43	0.37	0.39	0.19
2	0.44	0.40	0.42	0.20
3	0.44	0.40	0.42	0.21
5	0.46	0.44	0.45	0.24

for the exchanger prepared by the indirect fixation of 8-hydroxyquinoline to Separon H 40 E_{\max} .

This chelating ion exchanger establishes the sorption equilibrium rapidly both at low degrees of saturation (10%) and at a complete saturation (Fig. 1), owing to the hydrophilic nature of the macroporous matrix and location of the functional analytical groups predominantly on the particle surface; this is why the equilibrium establishes on this ion exchanger more rapidly than on the G-gel-based exchanger where the functional analytical groups occur within the whole particle bulk.

For assessing the suitability of the exchanger for the sorption of trace concentrations of heavy metals, the distribution coefficient of Cu^{2+} ions was determined at various pH values of solution (Fig. 2); the distribution coefficients of other heavy metals can be expected to be in the same relation to those of Cu^{2+} ions as on the other previously studied chelating ion exchangers with bonded 8-hydroxyquinoline¹. The distribution coefficient at low degrees of exchanger saturation (10% capacity) is rather high even in relatively acid solutions. The distribution coefficient (D_g) for Separon H 40 E_{\max} based ion exchanger is about 15 times higher than for the G-gel-based exchanger; the functional analytical groups of the former, located on the particle surface, are less rigid and thus make for an easier coordination of the metal, and moreover, the free coordination sites about the central metal atom can be

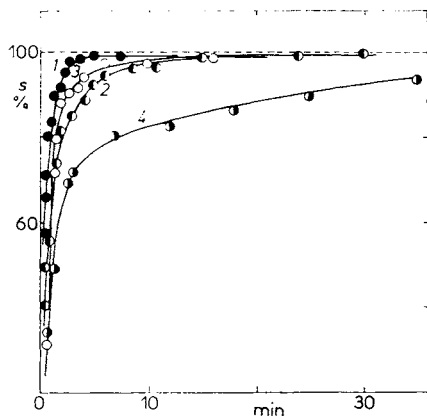


FIG. 1

Rate of establishment of the sorption equilibrium of Cu^{2+} ions (s) on ion exchangers prepared by the indirect fixation of 8-hydroxyquinoline to Separon H 40 E_{\max} (●, ○) and to G-gel (○, ●). Degree of saturation 10–15% (●, ○), saturated ion exchanger (○, ●)

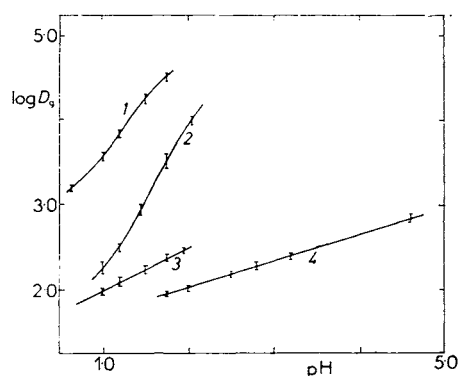


FIG. 2

pH-dependence of the distribution coefficient of Cu^{2+} ions (D_g) for Separon H 40 E_{\max} (1, 3) and G-gel (2, 4) based ion exchangers. Degree of saturation: 1, 2 10–15%, 3 85%, 4 65%

occupied more readily by solvent molecules, anions present, *etc.* The slope of the linear segment of the pH-dependence of $\log D_g$ is 1.5, which indicates roughly equal proportions of ML and ML_2 type complexes in the ion exchanger; this bears out the conclusion⁶ that for ion exchangers prepared by the indirect fixation, ML type complexes are also formed even at low degrees of saturation.

At an 85% degree of saturation, the expected decrease in D_g was observed. The slope of the linear segment of the $\log D_g$ vs pH plot is lower than 1; still, it is higher than with the G-gel-based ion exchanger, which indicates that on the Separon-based ion exchanger, nonselective sorption takes place to a lesser extent.

TABLE IV

Practical sorption capacities of the Separon H 40 E_{\max} based ion exchanger determined statically, after 24 and 48 h action of hydrochloric acid. Starting value $Q_a^{st}(Cu^{2+}) = 0.23 \text{ mmol g}^{-1}$

Time h	$Q_a^{st}(Cu^{2+}), \text{ mmol g}^{-1}$			
	1M-HCl	2M-HCl	3M-HCl	5M-HCl
24	0.22	0.22	0.21	0.21
48	0.21	0.21	0.20	0.19

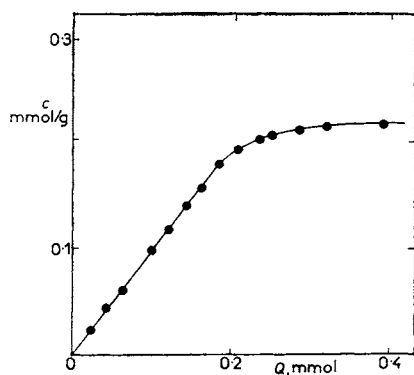


FIG. 3

Sorption isotherm of Cu^{2+} ions on Separon H 40 E_{\max} based ion exchanger at pH 4.6; c is the concentration of Cu^{2+} ions in the ion exchanger phase, Q is the amount of Cu^{2+} ions in solution

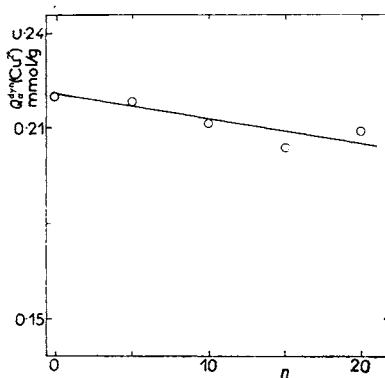


FIG. 4

Chemical stability of the Separon H 40 E_{\max} based ion exchanger with respect to cycling; n is the number of cycles

Owing to the high distribution coefficients along with the lower participation of nonselective sorption, the linear range of the sorption isotherm is rather wide, spanning about 80% of the sorption capacity (Fig. 3); hence, sorption from solutions of low concentrations is efficient even on the ion exchanger with a high fraction of occupied functional analytical groups.

The stability of the ion exchanger was tested by repeated sorption (Fig. 4) and by long-run action of dilute hydrochloric acid (Table IV). No loss of sorption capacity was observed after twenty sorption-elution cycles. No appreciable loss of capacity also occurred on a 24 h action of 1M to 5M-HCl; only in 48 h of action 3M or 5M-HCl the capacity decreased by 13% or 17%, respectively.

The Separon H 40 E_{\max} based chelating ion exchanger establishes the sorption equilibrium rapidly; especially noteworthy is the rapidity of the equilibrium establishment for the saturated exchanger. Although attempts to prepare an ion exchanger possessing a high sorption capacity failed, the ion exchanger obtained suits well to separations of trace concentrations of heavy metals. The exchanger sorbs strongly metal ions from very dilute solutions (high distribution coefficients) up to high degrees of saturation (wide linear span of the sorption isotherm). Its good stability enables the ion exchanger to be used repeatedly.

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