CHELATING ION EXCHANGERS WITH BONDED 8-QUINOLINOL ON A GLYCIDYL METHACRYLATE GEL

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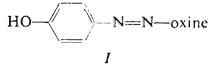
The optimum conditions of chemical bonding of 8-quinolinol to a porous glycidyl methacrylate matrix were established with respect to the sorption capacities of the ion exchangers prepared. After its modification, the reagent was fixed either directly as 5-(4-hydroxyphenylazo)-8-quinolinol or 5-(4-aminophenylazo)-8-quinolinol (or their copper(II) complexes), or indirectly, after fixing the intermediate and its diazotization, by coupling with the gel. The best results ($Q_a(Cu^{2+})$ = 0·24 mmol g^{-1}) were achieved by the direct bonding of copper 5-(4-hydroxyphenylazo)-8-quinolinate in pyridine.

Solid chelating ion exchangers have recently attracted interest. The properties demanded of such materials are above all a high selectivity (which is determined by the bonded analytical reagent) and a rapid establishment of the sorption equilibrium (dependent primarily on the properties of the maxtrix); an appropriate sorption capacity, given by the content of the fixed reagent and the way of its bonding, and a sufficient chemical stability are also desirable[1].

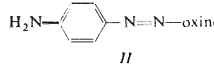
Up to now quite a number of chelating ion exchangers with various bonded reagents have been prepared. Among reagents most frequently used for this purpose is 8-quinolinol (8-hydroquinoline). Vernon[2,3] and Parrish[4] prepared such exchangers by polycondensation of 8-quinolinol, resorcinol, or phenol with formaldehyde. A resin has also been made up by polymerization of 5-vinyl-8-qionolinol[5]. The common way of fixing 8-quinolinol in various matrices is by azo bonding; ion exchangers based on polystyrene[7], silica gel[6], porous glass[8], cellulose[9,10], and glycol methacrylate resin[11] have been synthesized in this manner. The reagent has also been fixed to polystyrene *via* thiureide bonding or methylene bonding[12].

The aim of the present work was to seek for an optimum way of fixing 8-quinolinol, as the most thoroughly studied analytical reagent, to G-gel, a glycidyl methacrylate–ethylenedimethacrylate copolymer with a mass content of the former component of 63·2%; this gel[13] constituetes a macroporous hydrophilic matrix involving suitable reactive oxirane groups (3·5 mmol g^{-1}). 8-Quinolinol was fixed *via* a linking chain containing amino or hydroxy groups, readily attacking the oxidane ring; the connection of the reagent to the chain was accomplished by azo bonding[7]. The immobili-

zation of the reagent was achieved either by a direct fixation of the reagent and linking chain grouping *I* and *II* (or their copper(II) chelates), or by a three-stage synthesis in which the linking chain ($H_2N—C_6H_4—OH$ or $H_2N—C_6H_4—NH_2$) was fixed first and then diazotized and coupled to 8-quinolinol.



I



II

EXPERIMENTAL

5-(4-*Hydroxyphenylazo*)-8-*quinolinol* (I) was prepared by diazotization of 4-aminophenol[14] followed by coupling with 8-quinolinol[15]. The product was crystallized from dilute acetic acid and recrystallized from absolute ethanol. M.p. 237–239° (ref.[17] 239°C). For $C_{15}H_{11}N_3O_2$ (M_r = 265·3) calculated: 67·92% C, 4·18% H, 15·84% N; found: 67·8% C, 4·23% H, 15·9% N.

5-(4-*Aminophenylazo*)-8-*quinolinol* (II) was synthesized by diazotization of N-acetyl-1,4-diaminobenzene hydrochloride[16] followed by coupling with 8-quinolinol and by hydrolysis of the obtained 5-(4-(N-acetyl)-aminophenylazo)-8-quinolinol with dilute hydrochloric acid. The product was crystallized from 50% aqueous ethanol. M.p. 201–203°C (ref.[15] 206°C). For $C_{15}H_{12}N_4O$ (M_r = 264·3) calculated: 68·17% C, 4·57 H, 21·20% N; gound: 68·2% C, 4·49% H, 21·1% N.

The copper complexes of the 8-quinolinol derivatives were obtained by precipitation from solutions of 20 mmol of the derivative in 500 ml of 1M-NH_3 using 40 mmol of copper(II) chloride.

Bonding of 5-(4-*hydroxyphenylazo*)-8-*quinolinol to* G-*gel*. The procedure was analogous to the bonding of model enzyme structures to the gel[18]. To 0·55 g of the reagent in 10 ml of solvent were added 10 ml of a buffer solution or 0·2 g of a catalyst (Tables II, IV) and 0·25 g of G-gel[19] (particle size 65–130 μm, pore volume 1·21 ml g^{-1}, mean pore diameter 110 nm, specific surface area 27·5 m^2 g^{-1}, content of epoxy groups 3·5 mmol g^{-1}). The mixture, stirred with a nitrogen stream, was heated at 80°C for 24 h. The copper(II) complex of the reagent was fixed in the same manner. After the synthesis, the modified gel was washed with 25 ml of dimethylformamide, 25 ml of ethanol, and repeatedly with 10 ml of HCl, 25 ml of distilled water, and 10 ml of 2M-NH_3.

Bonding of 5-(4-*aminophenylazo*)-8-*quinolinol to* G-*gel*. The procedure was a modification of the bonding of glycine tert-butyl ester to epoxy groups-containing polymers[20] in aprotic medium using 4-nitrophenol as catalyst, or in ethanol under the catalytic effect of sodiumhydroxide[21].

Bonding of 4-*aminophenol or* 1,4-*diaminobenzene to* G-*gel, diazotization and coupling*. The intermediates constituting the linking chain were bonded in a similar way as *I* and *II*. The diazotization of aminophenyl-G-gel was performed by a modified procedure[9] in 5M-HCl using a triple excess of sodium nitrite. After 45 min, the diazotized gel was filtered out and used immediately for the coupling with 8-quinolinol[9]. The suspension was stirred by means of a nitrogen stream for 3 h.

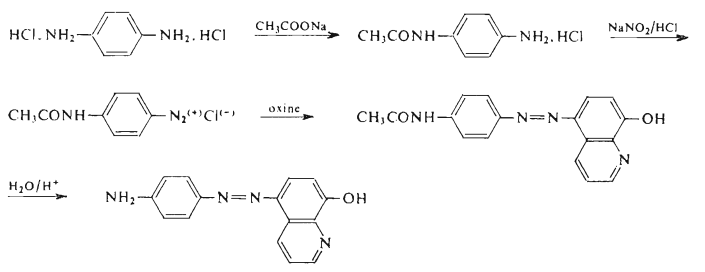
Determination of the exchange capacities. For the chelating ion exchangers prepared, both the theoretical exchange capacity corresponding to the content of the bonded analytical reagent (Q_g), established by determining the content of nitrogen, and the practical sorption capacity

with respect to Cu^{2+} ions ($Q_a(Cu^{2+})$) were determined. A sample of the ion exchanger tested (0·5 g) was washed with 10 ml of acetate buffer, pH 4·6, and 10 ml of 0·02M-$CuCl_2$ in the buffer solution was allowed to pass over the ion exchanger applying a flow rate of 1 ml min^{-1}. The Cu^{2+} ions in the eluate were determined spectrophotometrically as tetraammine copper(II) complex[22], the sorbed Cu^{2+} ions were eluted with 1M-HCl (10 ml) and determined spectrophotometrically with sodium diethyldithiocarbamate[22].

RESULTS AND DISCUSSION

The reactivity of the epoxy groups in G-gel enables the analytical reagent to be bonded to the matrixin different ways; the capacity of the resultant chelating ion exchangers is then also different. For the materials prepared, attention was paid particularly to their practical sorption capacity. The values derived from the data of the synamic sorption of Cu^{2+} ions and from the data of their elution from the exchanger were mutually consistent within the limits of experimental error. The relative error of the photometric determination was invariantly less than 5%. The relative standard deviation of the determination of the capacity for a given ion exchanger was less than 10% with the mean value of 6%, the relative standard deviation of the capacity determination for a series of exchangers prepared in an identical manner (hence, the reproducibility of synthesis) was always below 14%, the mean value was 10%. The results are given in Tables I–IV.

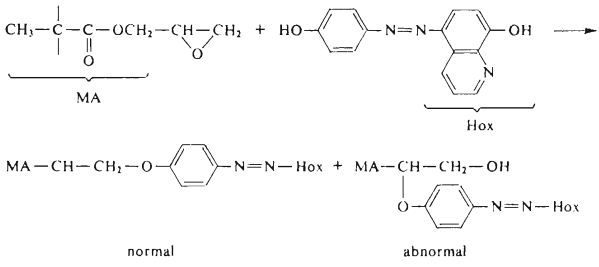
8-Quinolinol for the direct synthesis was modified in two ways. While no difficulties were encountered in the preparation of the 4-hydroxyphenyl derivative, in the synthesis of the 4-aminophenyl derivative (Scheme 1) the amino group had to be protected.



SCHEME 1

In this case during the diazotization and coupling, the diazonium salt was partly decomposed; consequently, the reaction yield was low and the reaction product crystallized poorly.

The 4-hydroxyphenyl derivative (*I*) was fixed as shown in Scheme 2. The first reaction step is cleavage of the oxirane ring. This process is acid or base catalyzed[23]; the degree of conversion in the noncatalyzed reaction is very low (Table I). Of the



SCHEME 2

solvents used, pyridine acting catalytically as a base led to the best results; ethanol and tetrahydrofuran suited as solvents too. Some nucleophilic solvents promote, in the conditions of the synthesis, the solvolysis of the epoxy ring; this effect, competing with the bonding of the reagent, is most pronounced in dimethylformamide, less in pyridine (less than 30% at pH 8·9), and is least marked in ethanol and tetrahydrofuran (less than 20%).

The ion exchangers prepared by acid catalyzed synthesis, analogous to the immobilization of model enzyme structures[18], exhibited very low practical sorption capacities

TABLE I

Effect of solvent on the bonding of 5-(4-hydroxyphenylazo)-8-quinolinol to G-gel

Solvent	Q_g(N) mmol g^{-1}	Q_a(Cu^{2+}) mmol g^{-1}	Remark
Dioxane	0·03	0·00	
Tetrahydrofuran	0·08	0·01	
Ethanol	0·06	0·02	
Acetone	0·03	0·00	
Dimethyl sulphoxide	0·04	0·01	
Dimethylformamide	0·11	0·00	solvolysis
Pyridine	0·61	0·07	general basic catalysis
Pyridine	0·25	0·01	in buffer pH 8·9 without substrate

(Table II). Also, for the acid catalyzed reaction there is a higher probability of formation of the „abnormal" product (Scheme 2) which is sterically less favourable for the formation of metal ion complexes than the normal product.

Specific opening of the epoxy ring giving rise to the normal product takes place in the base catalyzed process[23]. Ion exchangers synthesized under OH^- ion catalysis displayed a higher capacity only if the syntheses were carried out in a buffer with pH $\geq$ 9. Except for the synthesis catalyzed by sodium amide, the observed practical sorption capacities were several times lower than the theoretical capacities. This indicates that at lower pH values ($pK_2 = 9{\cdot}1$) the reagent is bonded to the gel preferentially *via* the hydroxy group of 8-quinolinol, whereupon the complex formation is precluded. In a more basic solution, protons are split off from both hydroxy groups ($pK_3 = 10{\cdot}6$), and the epoxy group is preferentially attacked by the $C_6H_4O^-$ group

TABLE II

Effect of catalysis on the bonding of 5-(4-hydroxyphenylazo)-8-quinolinol and its copper(II) complex to G-gel

Solvent[a]	Catalyst[a]	Buffer pH	Q_g(N) mmol g^{-1}	Q_a(Cu^{2+}) mmol g^{-1}
		Free reagent		
Ethanol	—	2·4	0·07	0·02
Dioxane	—	4·4	0·14	0·02
Pyridine	—	6·8	0·76	0·06
Pyridine	—	8·3	0·84	0·09
Pyridine	—	8·9	0·81	0·11
Pyridine	—	9·2	0·87	0·91
Ethanol	—	8·9	0·30	0·07
Dioxane	—	9·2	0·34	0·07
THF	TMAB	—	0·34	0·04
THF	TBAB	—	0·31	0·05
THF	$NaNH_2$	—	0·26	0·11
		Copper(II) complex		
Pyridine	—	—	0·73	0·24
Pyridine	—	8·2	0·49	0·18
Pyridine	—	8·9	0·49	0·14
DMF	$NaNH_2$	—	0·51	0·19

[a] Abbreviations: THF — tetrahydrofuran, TMAB — tetramethylammonium bromide, TBAB — tetrabutylammonium bromide, DMF — dimethylformamide.

as the stronger nucleophilic species. As a result, the practical sorption capacity at pH 8·3—9·2 increases, the theoretical capacity remaining constant (Table II). At higher pH values, however, the solvolysis of the oxirane ring also becomes more pronounced.

The synthesis was also catalyzed by means of common bases. Quaternary ammonium salts proved to be too weak bases to catalyze the reaction in question. When sodium amide was used the strongly basic medium caused a partial decomposition of the synthesized exchanger during its washing with water; good results were obtained by using alcohol for washing.

TABLE III

Bonding of 5-(4-aminophenylazo)-8-quinolinol and its copper(II) complex to G-gel

Reagent	Solvent	Catalyst	$Q_g(N)$ mmol g^{-1}	$Q_a(Cu^{2+})$ mmol g^{-1}
Free	mixed[a]	4-nitrophenol	0·11	0·05
Free	benzene	4-nitrophenol	0·39	0·09
Free	ethanol	NaOH	0·47	0·12
Copper(II) complex	benzene	4-nitrophenol	0·05	0·00

[a] Benzene–dimethylformamide mixture 4 : 1 (*V*/*V*).

TABLE IV

Capacities of ion exchangers prepared by three-stage synthesis

Fixed substrate	Solvent	Catalysis pH	$Q_{AM}(N)$[a] mmol g^{-1}	$Q'_g(N)$[b] mmol g^{-1}	$Q_a(Cu^{2+})$ mmol g^{-1}
4-Aminophenol	ethanol	(2·4)	1·49	0·70	0·09
4-Aminophenol	ethanol	(9·2)	—	0·83	0·12
4-Aminophenol	pyridine	(8·3)	1·76	0·84	0·09
4-Aminophenol	pyridine	(9·2)	1·52	0·92	0·10
1,4-Diaminobenzene	benzene	4-nitrophenol	1·65	1·00	0·20
1,4-Diaminobenzene	ethanol	NaOH	1·22	0·80	0·19

[a] Content of amino groups in the modified gel; [b] theoretical capacity calculated from the total nitrogen content, including the unreacted retained intermediates.

The use of the copper(II) complex of the 4-hydroxyphenyl derivative of the 4-hydroxyphenyl derivative (*I*) in the immobilization was promising in view of the spatial arrangement of the bonded molecules, corresponding to the most suitable configuration for a subsequent formation of metal ion complexes. Ion exchangers so prepared exhibited analytically usable practical sorption capacities; the decrease in the absolute amount of the bonded reagent corresponds to the higher steric requirements of the complex.

Bonding of the 4-aminophenyl derivative (*II*) did not yield results of practical interest. A benzene–dimethylformamide (4 : 1 vol.) mixed solvent was used to raise the solubility of the 4-aminophenyl derivative in the acid catalyzed reaction mixture. The addition of dimethylformamide, however, was found to lower the practical sorption capacity (Table III); synthesis in ethanol gave somewhat better results. The bonding of the copper(II) complex failed, probably because of a partial withdrawal of the lone electron pair from the amino group of copper(II) 5-(4-aminophenylazo)-8-quinolinate.

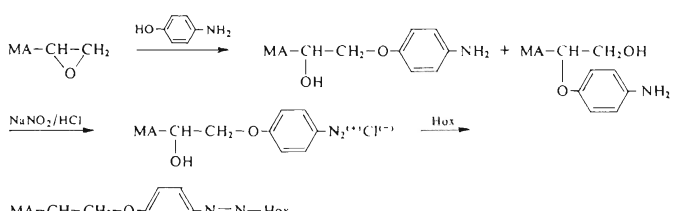
The three-stage synthesis, the first stage of which is the bonding of 4-aminophenol or 1,4-diaminobenzene to G-gel, is represented by Scheme 3. 4-Aminophenol is bonded well under base as well as acid catalysis (Table IV). The practical sorption capacities of the ion exchangers prepared from this intermediate were half as high as those of the preparations based on 1,4-diaminobenzene. In view of the high theoretical capacities, 4-aminophenol is likely to be bonded in part *via* the amino group. Thus, the procedure using 1,4-diaminobenzene is preferable; in this case the agent is bonded in a unique way, a simultaneous bonding of both amino groups being

TABLE V

Comparison of various ways of immobilization of 8-quinolinol on G-gel

Fixed derivative	Solvent	Catalysis (pH)	Q_g(N) mmol g^{-1}	$Q_a(Cu^{2+})$ mmol g^{-1}
HO—C_6H_4—N=N—Hox	ethanol	(2·4)	0·07	0·02
HO—C_6H_4—N=N—Hox	pyridine	(9·2)	0·87	0·19
HO—C_6H_4—N=N—Hox	THF	$NaNH_2$	0·26	0·11
HO—C_6H_4—N=N—Cuox[a]	pyridine	—	0·73	0·24
HO—C_5H_4—N=N—Cuox[a]	DMF	$NaNH_2$	0·51	0·19
NH_2—C_6H_4—N=N—Hox	benzene	4-nitrophenol	0·39	0·09
NH_2—C_6H_4—N=N—Hox	ethanol	NaOH	0·47	0·12
HO—C_6H_4—NH_2[b]	ethanol	(9·2)	0·83[c]	0·12
NH_2—C_6H_4—NH_2[b]	benzene	4-nitrophenol	1·00[c]	0·20

[a] Copper(II) complex; [b] three-stage synthesis; [c] corresponds to the Q'_g(N) value (Table IV).



The fixation of 1,4-diaminobenzene proceeds likewise.

SCHEME 3

unlikely on steric grounds. The low overall degree of conversion, 30–35% for the complete procedure, is accounted for by the hindered transport of molecules towards the epoxy groups within the gel and the low reactivity of the diazotized product. A good mixing of the heterogeneous reaction system is ensured by agitation during the diazotization and stirring with a nitrogen stream during the coupling. The stability of the fixed 1,4-diaminobenzene is satisfactory. The dry modified gel was stored in a bottle for 2 months and repeatedly used for the preparation of the ion exchanger without any loss in capacity.

The capacities of the products from the various processes of immobilization of 8-quinolinol are compared in Table V. The best results emerged from the direct bonding of the copper(II) complex of the 4-hydroxyphenyl derivative in pyridine; a drawback is the time-consuming final washing of the exchanger. For the other samples there appear high differences between the theoretical and the practical capacities, indicating a poor accessibility of the reagent for the chelation. Ion exchangers with a satisfactorily capacity resulted also from the three-stage synthesis *via* 1,4-diaminobenzene; this procedure is free from side reactions, the exchanger, however, contains a large amount of unreacted intermediates.

An advantage of both methods is their universality. Any analytical reagent of coupling as the passive component can be bounded in a similar way as 8-quinolinol. Higher exchange capacities cannot be so far expected.

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