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Hydrolysis of Oligosaccharides by Cation Exchanger Silica Gels

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Summary

Sulfonic acid cation-exchange resin usually synthesized from styrene divinylbenzene copolymers are not well effective as catalysts of oligosaccharides hydrolysis. The present paper deals with the rate of hydrolysis of oligosaccharides on a new cation exchanger obtained by grafting sulfonic groups on porous silica. With the large pore sizes, the sieving effect of large solutes is suppressed and the catalytic activity is comparable with that of polystyrenesulfonic acid in homogeneous phase.

INTRODUCTION

The hydrolysis of carbohydrates are generally easily catalyzed with the help of mineral acids, so polymer acids are expected to be efficient catalysts because of the higher local density of protons around the polymer chain than that in the bulk phase. Catalytic activity of polystyrenesulfonic acid (PSS) in the hydrolysis of sucrose has been shown by HARTLER and HYLLENGREN (1961). Compared with sulfonic acid, the polyelectrolyte splits sucrose 1.3 times more rapidly. PAINTER and MORGAN (1961) used polystyrenesulfonic acid as catalyst for the selective hydrolysis of polysaccharides.

In a previous work (HEYRAUD and RINAUDO (1981 a)), hydrolysis of dimers and trimer of D-glucose have been investigated. The relative reaction rates, based on SO_4H_2 (1.0), shown that polystyrenesulfonic acid had a slightly higher catalytic activity, depending on the type of dimer considered in the sequence of increasing selectivity maltose (1.5) < gentiobiose (1.6) < cellobiose (2.0). The effect was low and correlated to loose interaction between the substrate and the polyelectrolytes, but independant of the degree of polymerization (DP) ; so cross-linked sulfonated polystyrenes (ion-exchangers) have been used with the aim to perform hydrolysis of water soluble oligomers by a continuous process and to obtain the hydrolysed substrates without further purification. Various commercial ion-exchangers have been studied in a recent paper (HEYRAUD and RINAUDO (1981 b)). It was found that : (i) the rate of reaction was directly proportionnal to H^+ content ; (ii) the selectivity for the different types of dimers was in the same order as for PSS but the efficiency was depending on the

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morphology of the ion exchanger ; (iii) the rate of dimer hydrolysis was lower in the resin than with sulfuric acid and much more slower as the DP was increasing due to slow diffusion process. The sulfonic ion exchangers obtained by cross linkage of sulfonated polystyrene are not adapted to hydrolysis of oligosaccharides but now, new supports are available. The aim of this work is to show the capabilities of ion exchangers obtained by grafting sulfonic groups on porous silica ; rate of hydrolysis are compared with that obtained for catalysis by SO_4H_2 and polystyrenesulfonic acid.

EXPERIMENTAL

Materials : The Spherosil$^{(R)}$ S (sulfonated silica) were prepared by Rhône-Poulenc (France). The Duolite C204 F resin has been obtained from Diaprosim (France). The Amberlite IRN 77 resin was a commercial one. The average molecular weight of the polystyrenesulfonic sample was $Mw \simeq 200{,}000$. Maltose was a commercial sample ; the maltodextrins have been fractionnated by preparative GPC on Bio-Gel P2.

Hydrolysis of the oligomers : hydrolysis were carried out in batch ; 1 ml of solution of oligosaccharide (20 mg/ml) and 300-400 mg of dried ion-exchangers were put in 5 ml flask fitted with a reflux condenser and placed in a glycerol bath. Experiments with PSS and sulfonic acid were performed with 0.2 N solutions.

Kinetic studies : hydrolysis products were analysed by H.P.L.C. using Waters equipments ALC 201 and C-18 µ-Bondapak column eluted with water (HEYRAUD and RINAUDO, 1980).

The hydrolysis rate constants corresponding to the disappearance of the oligomer investigated have been directly determined from H.P.L.C. chromatograms according a procedure previously described (HEYRAUD and RINAUDO (1981 a-b)).

RESULTS AND DISCUSSION

We have compared five sulfonated silica with various porosities and two commercial sulfonic ion-exchangers with sulfuric acid and polystyrenesulfonic acid as references. The rate of hydrolysis of an oligomer S can be written :

$$V = k_{sp} \; [H_3O^+][S]$$

in which $[H_3O^+]$ is the average proton concentration in homogeneous as well as heterogeneous systems (HEYRAUD, RINAUDO, 1981 b).

Characteristics of ion exchangers and specific rate constants k_{sp} obtained in batch for maltose are summarized in Table I.

It is interesting to note that with silica, k_{sp} increases with porosity. With $\Phi \geqslant 600$ Å, the rate constant are higher than for sulfuric acid ; with Spherosil S_0 there is no difference between grafted silica and polystyrenesulfonic acid. So, with the highest porosity no limitating factor decreases the accessibility and the oligomer may interact with all

TABLE I : CHARACTERISTICS OF ION EXCHANGERS AND SPECIFIC RATE CONSTANTS (T = 70° C).

	ϕ pores (Å)	Wet mesh range	Capacity meq$[H_3O^+]$/g dry)	K_{sp} maltose $x10^3$ min^{-1}
* SPHEROSIL S_O	3000	-	0.31	2.1
SPHEROSIL S	1250	-	0.48	1.5
SPHEROSIL S_1	600	-	0.63	1.4
SPHEROSIL S_2	300	-	0.83	0.9
SPHEROSIL S_3	80	-	1.36	0.8
AMBERLITE IRN 77	-	20-50	3.7	0.3
DUOLITE C 204 F	-	20-50	2.9	0.8
H_2SO_4	-	-	-	1.3
PSS	-	-	-	2.0

*SPHEROSIL S_o, S_1, S_2, S_3 are experimental samples.

TABLE II : HYDROLYSIS RATE CONSTANTS OF MALTODEXTRINS (T = 70° C)

DP K_{sp} $x10^3$ mn^{-1}	2	3	4	5
$K_{sp} H_2SO_4$	1.3	1.9	2.5	3.2
K_{sp} PSS	2.0	3.0	4.1	-
K_{sp} IRN 77 (8% DVB)	0.3	0.3	-	-
K_{sp} Duolite C 204 F (3-6 % DVB)	0.8	0.9	0.9	0.7
K_{sp} SPHEROSIL S_3 ϕ= 80 Å	0.8	2.0	2.0	1.8
K_{sp} SPHEROSIL S_o ϕ= 3000 Å	2.1	2.8	3.4	3.9

available ionic sites. This point is very important and complementary studies with oligosaccharides of higher DP have been achieved. The results are given in Table II.

The catalytic activity of cation exchangers on hydrolysis of maltodextrins differs markedly in the presence of matrix with different structures. For gel ion exchangers, the reaction rate constant depends on divinylbenzene content (% DVB) and decreases with increasing degree of crosslinking. So, hydrolysis rate constant of maltose is higher with Duolite C 204 F. Meanwhile, whatever the resin may be, gel ion exchangers contain cavities with diameter < 80 Å and hydrolysis of upper DP is affected owing to a sieving effect. By using silica, an usual support in gel permeation chromatography, oligosaccharides penetrate easily into the pores and with a large pore size silica there is no limitating factor.

CONCLUSION

Ion exchangers obtained by grafting sulfonic groups on silica have been demonstrated to have catalytic properties more interesting than gel cation-exchange resins in hydrolysis of oligosaccharides . Silica allows to use matrices with large pore sizes so with an appropriate diameter there is no sieving-effect and oligomers react as with polystyrenesulfonic acid. Such support may be useful with water soluble polysaccharides by performing a continuous hydrolysis with a good efficiency in a column process.

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