CHROM. 23 858

Chromatographic separation of polyols by ligand exchange

Effects of the ion-exchange resin cross-linking and size

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ABSTRACT

The influence of the degree of ion-exchange resin cross-linking and size on the resolution and purity of products separated by ligand-exchange liquid chromatography was studied with mannitol–sorbitol and arabitol–xylitol mixtures. The experiment was carried out with seven calcium resins. The best results (90% recovery of pure mannitol and sorbitol and 80% recovery of pure arabitol and xylitol) were obtained with an average size of 25 μm and 7% cross-linking.

INTRODUCTION

Extraction by water diffusion, hydrolysis or pressing of plant materials produces sugar mixtures. Catalytic [1] or enzymatic [2] hydrogenation of these mixtures yields polyol mixtures. Chromatography using cation-exchange resins and water as the eluent makes it possible to separate different components of these mixtures and therefore, favours their utilization. The separations depend on the complex-formation equilibria between carbohydrates and the resin counter-ions. In this case chromatography is called ligand exchange. Many works deal with this topic, such as those by Angyal *et al.* [3] and Goulding [4]. Apart from the chemical equilibria involved in the formation of sugar–cation complexes, for which the choice of the resin counter-ion is important [5], many parameters influence the efficiency of a chromatographic separation:

(i) The accessibility of the resin sites for ligand exchange. This depends on the pore size of the support. In the case of gel ion-exchange resins, accessibility will depend on the degree of cross-linking of the polymer matrix expressed as a weight percentage of divinylbenzene (DVB).

(ii) The dispersion of molecules to be separated in relation to the path differences in the chromatographic column. The dispersion depends on how the column is packed and on the particle size.

In order to optimize the chromatographic separation of two industrial mixtures on a ion-exchange resin in the calcium form, the influence of the degree of cross-linking and size of the support were studied. The two mixtures tested were:

Mannitol–sorbitol obtained from the catalytic hydrogenation of fructose [6],

Arabitol–xylitol obtained from the hydrogenation of fibre plant hydrolysates [7].

Although various models have been used to predict the effects of different factors (dispersion in the eluting phase, external resistance to mass transfer around particles, internal diffusion in the stationary phase) [8–10], none presents a direct and simple correlation with the support characteristics.
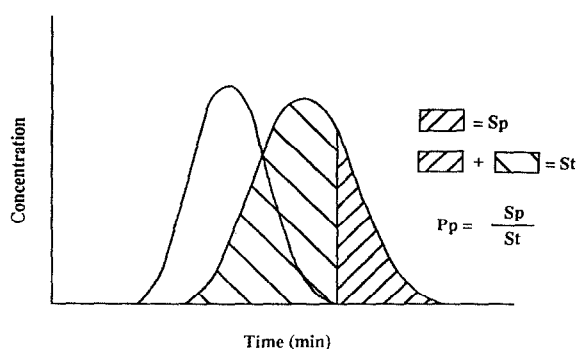
Fig. 1. Definition of recoverable pure product.

Fig. 2. Definition of resolution.

The experimental design set-up allows the determination of a polynomial correlation involving reticulation, resin average size and separation efficiency. This efficiency is controlled through yields of recovered pure products, P_p (Fig. 1), and resolution, R (Fig. 2).

EXPERIMENTAL

A 200 cm × 1.67 cm I.D. glass column maintained at 50°C by fluid circulation in the jacket was packed with calcium Purolite resin (PCR) a chosen size and degree of cross-linking by progressive water sedimentation. The characteristics of the gel resins are shown in Table I. Products used to reconstitute polyol mixtures to be separated were commercial products from Fluka (mannitol, xylitol), Aldrich (sorbitol) and Extrasynthese (arabitol). Mixtures were recombined in deionized water (resistivity
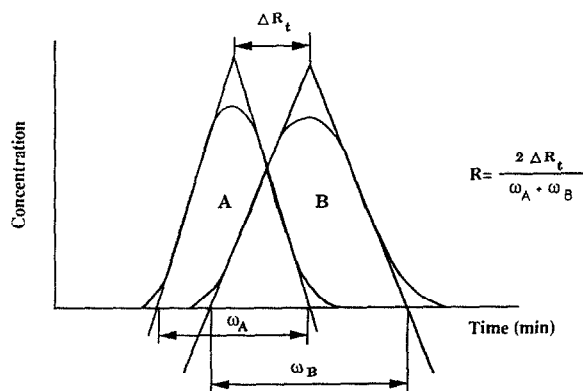
above 10 MΩ cm). The concentration of each constituent of the mixture was 50 g/l. A 1.5-cm³ volume of the solution to be separated was directly injected onto the resins at the top of the column. To prevent the injected solution from being diluted, water elution was only started when the total solution had penetrated the resin. A Gilson Minipulse 2 peristaltic pump fed the system with eluent (deionized water) at 50°C. A Gilson MTDC automatic fraction collector recovered the effluent at the column outlet. At the end of the separation, the collected fractions were analysed by high performance liquid chromatography (HPLC) on an LDC Milton Roy III device coupled with a refractometric detector equipped with a data base. These analyses made it possible to draw the chromatogram for the separation obtained at the column outlet.

TABLE I

CHARACTERISTICS OF GEL RESINS

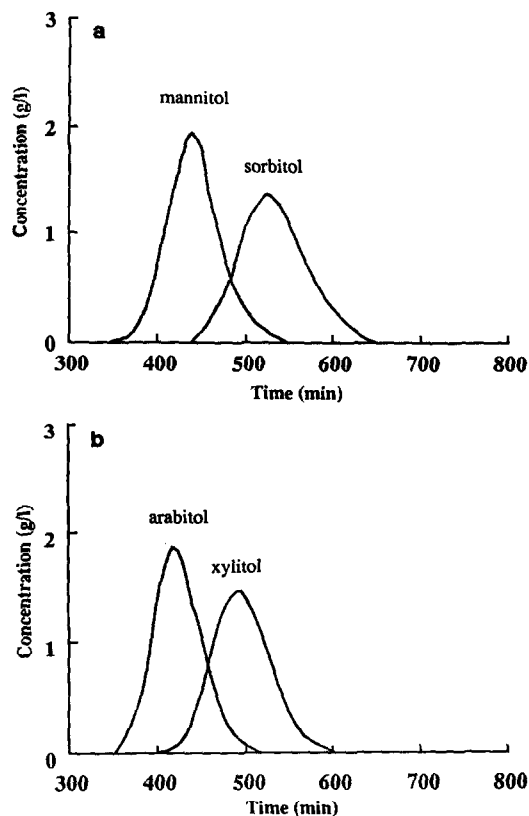| PCR	DVB (%)	Total capacity (equiv./l H⁺)	Humidity (% H⁺)	Particle size (μm)	
				Mean	Range (90%)
833	7.6	1.80	51–55	225 ± 25	150–300
853	7.6	1.55	57–61	350 ± 25	275–425
453	4.7	1.20	64–67	350 ± 25	275–425
433	4.7	1.55	57–61	225 ± 25	150–300
593	5.9	1.20	64–67	525 ± 25	150–300
533	5.9	1.80	51–55	225 ± 25	275–425
553	5.9	1.55	57–61	350 ± 25	450–600

Fig. 3. (a) Separation of mannitol–sorbitol on PCR 593 Ca. Flow-rate: 0.95 ml/min. (b) Separation of arabitol–xylitol on PCR 593 Ca. Flow-rate: 1.0 ml/min.
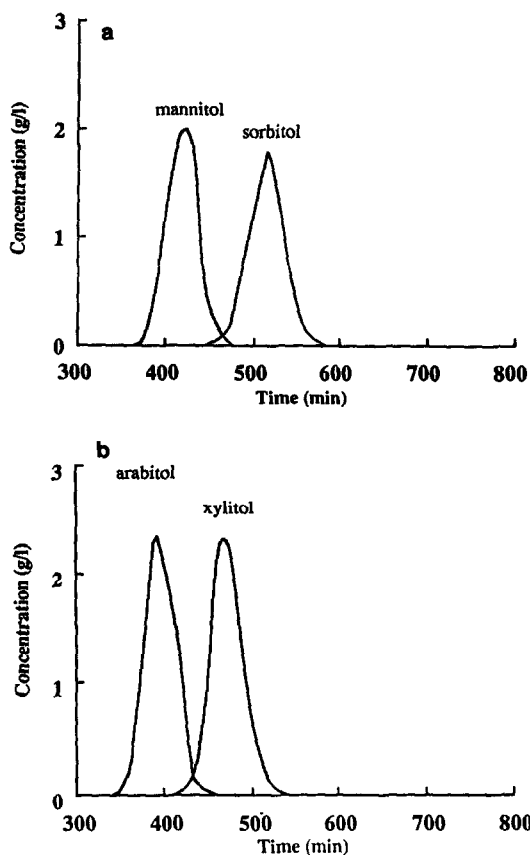
Fig. 4. (a) Separation of mannitol–sorbitol on PCR 533 Ca. Flow-rate: 1.0 ml/min. (b) Separation of arabitol–xylitol on PCR 533 Ca. Flow-rate: 1.0 ml/min.

TABLE II

EXPERIMENTAL RESULTS OF THE TWO STUDIED RESPONSES

PCR	$^a R_{MOH–SOH}$	$^b R_{XOH–AOH}$	$^c P_{p\,MOH}$ (%)	$^d P_{p\,SOH}$ (%)	$^e P_{p\,AOH}$ (%)	$^f P_{p\,XOH}$ (%)
833	1.01	1.00	94	82	83	75
853	0.78	0.68	24	28	20	28
453	1.09	0.93	75	43	54	34
433	0.73	0.47	46	42	21	22
593	0.67	0.60	11	31	22	20
533	1.30	1.05	91	87	69	72
553	0.85	0.69	58	63	41	64

^{a} Resolution of mannitol–sorbitol separation.
^{b} Resolution of arabitol–xylitol separation.
^{c} Pure mannitol recoverable.
^{d} Pure sorbitol recoverable.
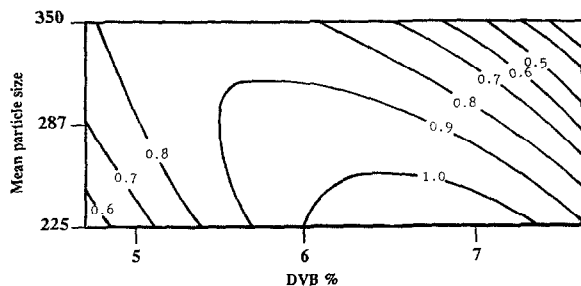^{e} Pure arabitol recoverable.
^{f} Pure xylitol recoverable.

Fig. 5. Isoresponse curves of the resolution of mannitol–sorbitol separation as a function of degree of cross-linking and resin particle size (in μm).
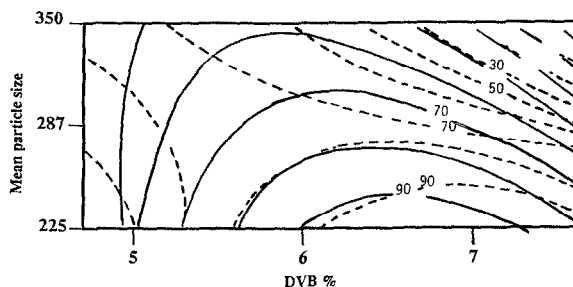

Fig. 7. Isoresponse curves of pure mannitol (broken lines) and sorbitol (solid lines) yield. Mean particle size in μm.
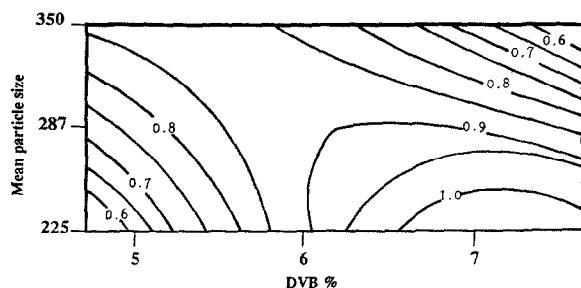

Fig. 6. Isoresponse curves of the resolution of arabitol–xylitol separation as a function of degree of cross-linking and resin particle size (in μm).
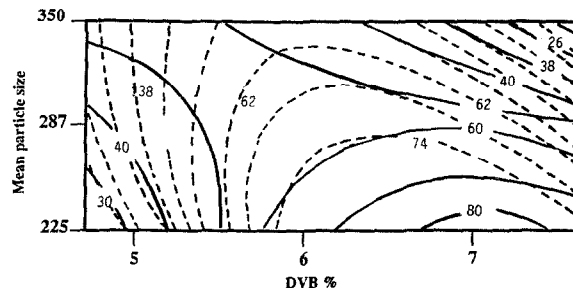

Fig. 8. Isoresponse curves of pure arabitol (solid lines) and xylitol (broken lines) yield. Mean particle size in μm.

RESULTS AND DISCUSSION

Separation chromatograms (Figs. 3 and 4) obtained with each resin allow calculation of the two responses studied (Table II). The analysis of isoresponse curves, drawn by calculating coefficients of the second-degree polynomial model [11], indicates that:

(i) With a degree of cross-linking averaging 5%, an increase in the resin size favours resolution (Figs. 5, 6) and higher yields of pure products. This has been already noted in the separation of glucose–fructose with the same type of resins [12].

(ii) With high degrees of cross-linking (>6% DVB), a decrease in the resin size favours resolution. Such results have already been noted in xylose–mannose separations [13] using Duolite resins C 204 in the Pb^{2+} form with a 5.5–6.5% DVB cross-linking. The best yields of pure products, 90% mannitol and sorbitol and 80% arabitol and xylitol, were achieved with a degree of cross-linking averaging 7

DVB and an average size of 225 μm (Figs. 7 and 8).

These results show how complex is the effect of cross-linking on the phenomena involved in a separation.

An increase in the degree of cross-linking results in an increase in the capacity of the chromatographic column. This should lead to an improvement in capacity factors (k') and, therefore, a better separation. However, after calculating k', no systematic correlation could be determined (Figs. 9 and 10). Indeed, increased in cross-linking corresponds to decreased humidity, which leads to reduced resin swelling. Penetration of molecules to be separated inside the resin, towards complexing sites, is then favoured. Likewise, depending on the nature of the molecules and cross-linking, this restriction could be more or less important than the positive effect of an increase in capacity.

Models reported up until now do not take into account variations in the resin swelling during the passage of substrate. Variations in the height of the
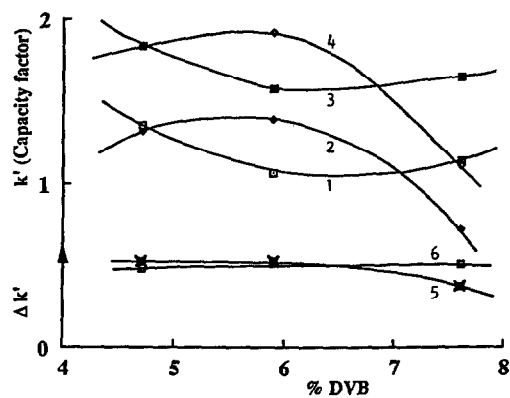
Fig. 9. Influence of the degree of cross-linking on the capacity factor of mannitol and sorbitol. Curves: 1 = k' mannitol 350; 2 = k' mannitol 225; 3 = k' sorbitol 350; 4 = k' sorbitol 225; 5 = $\Delta k'$ sorbitol−manitol 225; 6 = $\Delta k'$ sorbitol−mannitol 350. The values 350 and 225 indicate the mean particle size (μm) (Table I).

Fig. 10. Influence of the degree of cross-linking on the capacity factor of arabitol and xylitol. Curves: 1 = k' arabitol 225; 2 = k' arabitol 350; 3 = k' xylitol 225; 4 = k' xylitol 350; 5 = $\Delta k'$ xylitol−arabitol 225; 6 = $\Delta k'$ xylitol−arabitol 350. The values 350 and 225 indicate the mean particle size (μm) (Table I).

chromatographic column bed have been experimentally observed. These variations may be responsible for the larger dispersion, resulting in peak widening and a lower resolution.

The positive effect of an increase in degree of cross-linking could be explained by a lower sensitivity of the resin towards swelling phenomena.

CONCLUSIONS

It is clear that the effect of the degree of cross-linking is hard to determine. Indeed, its increase leads to:

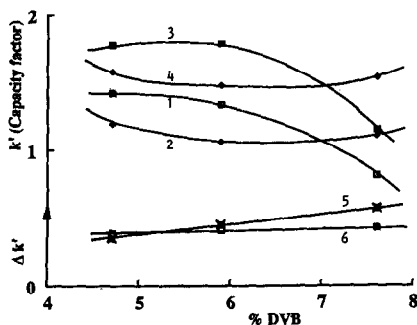(i) A higher capacity through a larger number of complex sites on an equally sized column.

(ii) A restricted dispersion of molecules to be separated through a lower swelling sensitivity when substrates pass down the columns.

However these two positive effects are restricted by the diffusion of molecules into the resin.

The influence of the resin size seems to be linked to that of the degree of cross-linking since isoresponse curves indicate that there are two opposite ways of improving separation.

According to these results and those of Welstein and Sauer [12], the selection of the support characteristics should depend on yield and purity of expected products. In the case of polyols, a small-sized resin (225 μm) with 7% DVB should be selected, whereas a larger sized resin (about 400 μm) with a 6% DVB cross-linking should be used to separate glucose–fructose mixtures.

TABLE III

CAPACITY FACTORS (k') FOR THE DIFFERENT COMPONENTS SEPARATED ON PUROLITE RESINS ELUTING WITH WATER

PCR	DVB	Particle	k' arabitol	k' xylitol	$\Delta k'_1$	k' mannitol	k' sorbitol	$\Delta k'_2$
833	7.6	225	1.32	1.90	0.58	0.73	1.11	0.38
853	7.6	350	1.11	1.55	0.44	1.14	1.66	0.52
453	4.7	350	1.19	1.58	0.39	1.35	1.84	0.49
433	4.7	225	1.42	1.78	0.36	1.31	1.84	0.53
593	5.9	525	1.40	1.84	0.44	1.38	1.89	0.51
551	5.9	350	1.15	1.59	0.44	1.38	1.92	0.54
553	5.9	350	1.06	1.48	0.42	1.06	1.58	0.52
533	5.9	225	1.34	1.80	0.46	1.39	1.92	0.53

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