

CHROM. 5968

Chromatography of alcohols and sugars on Fe (III)-loaded cation-exchange resin

The chromatography of sugars, and polyhydric alcohols on ion-exchange resins is well known^{1,2}. Good separations are achieved with anion- and cation-exchange resins carrying a variety of counter-ions. Ethanol-water mixtures containing 85–95 % of ethanol are good eluents. The mechanism of retention is not well understood, but it seems to be related to the preferential absorption of water by the resins. The water:ethanol ratio is considerably higher in the resin than in the solution that surrounds it, and sugars are more soluble in water than in ethanol.

In cation-exchange resins with alkali metal counter-ions the absorption of sugars and polyhydric alcohols generally increases in the order $\text{Li} < \text{Na} < \text{K}$. This order reflects decreasing ionic hydration and hence increasing availability of the resin water to dissolve the sugars.

Our work on ligand-exchange chromatography^{3,4} led us to ask whether resins carrying metal ions, such as Fe(III), which form hydroxy-complexes would act as absorbents for polyhydric alcohols and sugars. Preliminary tests with the sulfonated polystyrene-divinylbenzene resin Dowex-50, carrying Cu(II), Fe(III) Th(IV), were negative. The lack of retention could have been due to the low swelling of the resin in 90–95 % alcohol. We therefore tried the macroporous polystyrene-based cation-exchange resin, Amberlyst-15, manufactured by the Rohm and Haas company. It gave good retention of ethylene glycol, glycerol and sorbitol, and good discrimination between them, using absolute methanol as the eluent. Absolute ethanol gave considerably greater retention of ethylene glycol and glycerol⁵. It could not be used with sorbitol because of the very low solubility of sorbitol in 100 % ethanol.

This note reports studies with the Fe(III)-loaded macroporous resin Amberlyst-15, with methanol and ethanol eluents.

Experimental

The resin Amberlyst-15 was first washed with dilute hydrochloric acid (HCl) and water in a large preparatory column. A solution 0.2 M in ferric nitrate and 0.4 M in HCl was passed to saturation. The resin was washed with 50 % aqueous methanol followed by 100 % methanol, then removed from the column and air dried, ground and screened, collecting the 50–100 mesh fraction. This was stirred with absolute methanol and packed into a column 0.9 cm I.D. to form a bed 82 cm long. Tests were also made with a bed 25 cm long.

The glass column and its fittings, including an injection valve, were supplied by Chromatronix, Inc. Solvent was contained in a stainless steel cylinder and driven under pressure by helium. The detector was a Waters Associates differential refractometer coupled with a Leeds and Northrup 50-mV recorder. The flow-rate was normally 60 ml per h, and the samples introduced had 1 mg of the solute in 0.1 ml of the same solvent that was used as eluent.

Results and discussion

Table I gives the elution volumes of a number of solutes, and Fig. 1 shows three representative refractometer curves. That the refractometer peaks actually corresponded to the elution of the substances indicated was demonstrated by collecting the eluate fractions and evaporating them. The peak for water is noteworthy; first, water in low concentrations raises the refractive index of methanol instead of lowering it; second, the fact that the retention volume of water in 100% methanol eluent was so large, demonstrates that the resin was not saturated with water,

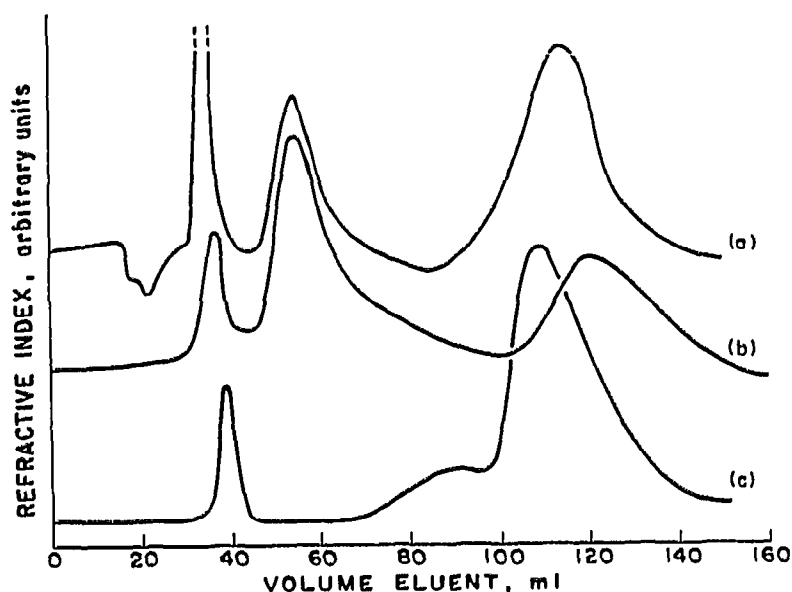


Fig. 1. Elution curves for representative mixtures. Column, Fe(III)-Amberlyst-15, 0.9 cm \times 82 cm. Eluent, absolute methanol. Elution orders: curve (a), acetone, ethylene glycol, pentaerythritol; (b), ethanol, glycerol, sorbitol; (c), isopropyl alcohol, mannitol, water.

TABLE I

ELUTION VOLUMES ON MACROPOROUS Fe(III)-LOADED RESIN

Column 0.9 cm \times 82 cm; flow rate 60 ml/h.

Compound eluted	Solvent		
	Ethanol 95%	Methanol 100%	Methanol 95%
Ethanol	—	40	44
Acetone	—	40	—
Isopropanol	38	39	—
<i>tert.</i> -Butyl alcohol	—	40	—
Sucrose	60	45	44
Glucose	—	45	—
Ethylene glycol	67	54	44
Glycerol	75	57	—
Mannitol	100 ^a	92	—
Water	59	107	—
Sorbitol	—	118	57
Pentaerythritol	85	114	—

^a Mannitol peak with 95% ethanol showed much tailing.

and that the small amount of water added to the methanol competed effectively with methanol for absorption sites on the resin. These "sites" presumably included coordination sites on Fe (III).

A little water had to be added to help mannitol, sorbitol and pentaerythritol dissolve in methanol. The water emerged from the column as a separate, distinguishable peak.

In agreement with the work of SAMUELSON *et al.*^{1,2}, polyhydric alcohols are retained more strongly the greater their molecular weights and the more hydroxyl groups they carry. In contrast to their work, however, we find that hexahydric alcohols derived from sugars are retarded much more strongly than hexose sugars. Ethanol gives much more retention than methanol, but in our method, even more than in SAMUELSON's, the proportion of water in the eluent has a large effect, and we find that the water content must be below 5 % for good results. Then we encounter the difficulty that the higher alcohols have a very low solubility.

It seems that the Fe(III) ions in the resin do associate with the hydroxy compounds, but their solvation energies with water and methanol are so great that it is difficult to achieve the conditions of balance that give good chromatographic separation. The use of Fe(III)-loaded resins offers no advantages over that of cation-exchange resins loaded with alkali metal ions, except for the fact that they bind polyhydric alcohols much more strongly than the corresponding sugars.

We gratefully acknowledge support of the U.S. National Science Foundation through its Summer Research Participation Program for College Teachers and indirectly through Grant No. GP-25727.

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Received February 7th, 1972

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