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## Note

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### Dissociation of sulphonic acids sorbed onto a non-polar stationary phase

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Non-polar stationary phases have increasingly become important for separation of anions in eluents containing quaternary ammonium ions with non-polar substituents, and of cations in the presence of hydrophobic anions such as alkyl sulphonates<sup>1,2</sup>. In some systems ion-pair formation may occur in the external solution and the term ion-pair chromatography is then justified. The quaternary ammonium salt and the sulphonate are enriched in the stationary phase which will behave as an anion exchanger or cation exchanger, respectively. The term "dynamic ion-exchange chromatography" has sometimes been used<sup>3</sup>, but since chromatography is itself a dynamic process the authors prefer the term "chromatography on sorbed ionic sites"<sup>4</sup>.

The free-acid form of a cation-exchange resin of the sulphonic acid type is virtually completely dissociated<sup>5</sup>. This has been demonstrated by studies of cation-exchange equilibria and reactions catalyzed by hydrogen ions. To determine whether hydrophobic electrolytes adsorbed on non-polar stationary phases are dissociated, we have studied the inversion of sucrose in aqueous solution by means of anthraquinone-2-monosulphonic acid (AMS) sorbed on a macroporous styrene-divinylbenzene resin, Hitachi gel 3011.

#### EXPERIMENTAL

The styrene-divinylbenzene resin (Hitachi 3011, Hitachi, Tokyo, Japan) had a particle size of  $12 \pm 5 \mu\text{m}$ . It was packed into a jacketed steel column (100 × 5 mm) as described previously<sup>4</sup>. The breakthrough curves for AMS were calculated from absorbance measurements at 280 nm. The column was treated with 25% (w/w) ethanol to replace adsorbed AMS, and carefully washed with water before the curves were recorded. The inversion of sucrose was studied by passing aqueous solutions through this column.

The effluents were analyzed by partition chromatography in 75% ethanol on the sulphate form of an anion-exchange resin<sup>6</sup>. The temperature was 75°C. The calculations were based on determinations of glucose in the eluate. For experiments with large degrees of inversion, the decrease in sucrose concentration was in good agreement with that calculated from the formation of glucose.

## RESULTS AND DISCUSSION

The sorption of AMS onto the Hitachi gel was studied by recording the breakthrough curves at room temperature. As shown in Fig. 1, AMS was strongly retained by the resin. The breakthrough capacity calculated in bed volumes of the solution decreased by approximately 50% when the influent concentration was increased by a factor of ten. When the column was saturated with AMS ( $C/C_0 = 1$ ), the total amount of AMS in the column (calculated from the area between the breakthrough curve and the ordinate) was 5 mmol per litre of bed volume when the influent solution contained  $0.1 \text{ mmol l}^{-1}$ . At a ten-fold influent concentration the total amount of AMS was  $23 \text{ mmol l}^{-1}$ .

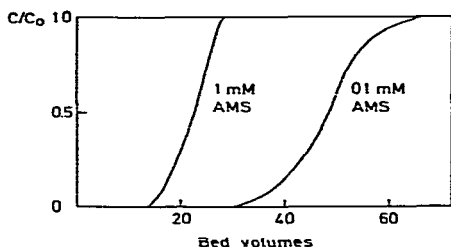


Fig. 1. Breakthrough curves recorded at room temperature for aqueous solutions of AMS containing 10 mmole of sucrose per litre. Nominal linear (empty tube) flow-rate:  $5.0 \text{ cm min}^{-1}$ .

Evidently, the adsorption isotherm was non-linear within this concentration range. The increase in concentration resulted in a decrease in the distribution coefficient by approximately 55%. The ambiguity in the determination of the interstitial volume makes it impossible to calculate accurately the average concentration of AMS in the stationary phase, but it is reasonable to assume that this concentration was approximately  $10 \text{ mmol l}^{-1}$  at the lower concentration of AMS, and  $50 \text{ mmol l}^{-1}$  at the higher.

Inversion experiments were made on a column packed with Hitachi gel and conditioned with  $0.1 \text{ mM}$  AMS in  $10 \text{ mM}$  sucrose solution at  $90^\circ\text{C}$ . The inversion was approximately 3% at a nominal linear flow of  $2.5 \text{ cm min}^{-1}$ . In a blank in which the same solution was heated in the absence of resin the inversion was less than 0.3%.

The concentration of AMS in the solution was then increased by a factor of ten. As shown in Fig. 2 this led to a markedly increased inversion of sucrose. The

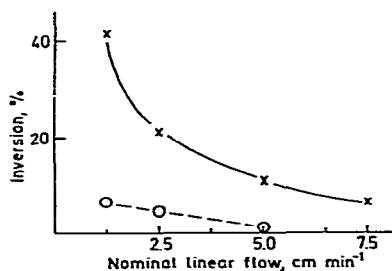


Fig. 2. Percentage inversion at  $90^\circ\text{C}$  of  $10 \text{ mM}$  sucrose solution as a function of the nominal linear flow-rate. The broken line refers to the inversion for blanks in  $1 \text{ mM}$  AMS without any resin present, recalculated on the assumption that the relative interstitial volume was 0.5 in the column packed with resin.

inversion was much higher than in blanks carried out in the absence of the Hitachi gel. Finally, blanks were made with the Hitachi gel without the presence of AMS. No formation of glucose was observed.

The results show that AMS adsorbed on a non-ionic stationary phase exerted a large catalytic effect on the inversion of sucrose. We conclude that the adsorbed sulphonic acid was dissociated and that the hydrogen ions present as counter ions in the stationary phase were responsible for the large inversion of sucrose. It is believed that in many other chromatographic systems with water as the predominant solvent, and with sulphonates or quaternary ammonium salts present in the eluent and enriched in the stationary phase, the ions in the stationary phase are dissociated. In such systems the term ion-pair chromatography may lead to misunderstanding. It is suggested that it is replaced by the term "chromatography on sorbed ionic sites". Additional arguments were given previously<sup>4</sup>.

#### REFERENCES

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