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## INVESTIGATION OF ANION-EXCHANGE EQUILIBRIA OF MALEIC AND FUMARIC ACIDS

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### SUMMARY

The effect of pH on the distribution coefficients of maleic and fumaric acids on Dowex 1-X8 ( $\text{Cl}^-$ ) anion-exchange resin has been investigated. From the dependence of the overall distribution coefficient on the pH of the solution, the ion-exchange selectivity coefficients for the monovalent and bivalent anions of maleic and fumaric acids have been calculated. The selectivity series observed follows the decreasing order of protonation constants. The nuclear magnetic resonance spectra of the resin in various ionic forms have also been investigated qualitatively.

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### INTRODUCTION

Chromatography on anion-exchange resins in the hydroxide, chloride, nitrate, acetate, borate, sulphate and carbonate forms has been widely used for the separation of organic acids. The various methods have been reviewed recently by Jandera and Churáček<sup>1</sup>. Relatively few data are available, however, for the selectivity coefficients of *cis-trans* isomeric dicarboxylic acids. A study of the anion-exchange behaviour of maleic and fumaric acids was therefore undertaken in an attempt to obtain more information about the factors underlying the selective sorption of these acids on an ion-exchange resin in the chloride form.

### EXPERIMENTAL

Dowex 1-X8 ( $\text{Cl}^-$ ), 100–200 mesh, ion-exchange resin was obtained from Serva (Heidelberg, G.F.R.). The weight capacity of the resin was determined by the standard column technique<sup>2</sup>.

A  $10^{-1}$  M stock solution of maleic acid and a  $2 \cdot 10^{-2}$  M stock solution of fumaric acid were prepared from reagent-grade chemicals. The pH values of these solutions were adjusted by the following method. A 20-ml volume of 0.5 M hydrochloric acid was pipetted into a 100-ml calibrated flask. For the investigation of the equilibrium of maleic acid 10 ml, and for fumaric acid 50 ml, of the above stock solution were added to the calibrated flask. Before filling the flask to the mark with distilled water, the required volume of saturated sodium hydroxide solution was added to it.

The overall distribution coefficients were measured by a batch method. A 50-ml volume of the above mixture was added to 0.5 g of the resin in a 100-ml glass-stoppered flask and allowed to stand with intermittent shaking for 24 h at room temperature. After the attainment of equilibrium, the final pH of the solution was determined by using a glass electrode.

After the liquid phase had been filtered free from the resin, an aliquot of the liquid was analyzed for the organic acid present. The distribution coefficient was calculated from the difference in concentration of organic acid before and after attainment of equilibrium. The concentration of the organic acid was determined by the polarographic method described by Elving and Rosenthal<sup>3</sup>.

Nuclear magnetic resonance (NMR) spectra were obtained with a Varian A-60 spectrometer. The chloride form of the resin was converted into the desired ionic form by a standard column procedure. For the conversion, the pH of a  $10^{-1} M$  solution of maleic acid was adjusted to 3.9 or 10.0 and that of  $2 \cdot 10^{-2} M$  fumaric acid to 3.8 or 7.65. After conversion, the resin was carefully air-dried and the dry resin was transferred into an NMR tube filled with a solution of appropriate concentration. The weight ratio of the resin and solution was approximately 1:1.

## RESULTS AND DISCUSSION

The overall distribution coefficients were calculated using the following equation:

$$D = \frac{\text{amount of acid on resin}}{\text{amount of acid in solution}} \cdot \frac{\text{ml of solution}}{\text{g of dry resin in chloride form}}$$

The calculated distribution coefficients for maleic and fumaric acids are plotted against the pH in Fig. 1.

For the calculation of the ion-exchange selectivity coefficients, the following equation was derived earlier<sup>4</sup>:

$$D = \frac{K_{BH}^x K_1 Q [H^+] [Cl^-]^{-1} + K_B^x Q^2 [Cl^-]^{-2}}{1 + K_1 [H^+] + K_1 K_2 [H^+]^2}$$

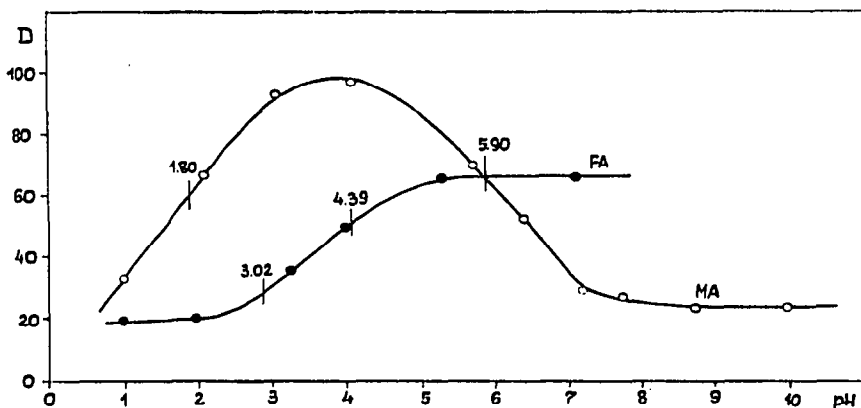


Fig. 1. Change of the distribution coefficients of maleic and fumaric acids as a function of pH. Resin: Dowex 1-X8.  $c_{MA} = c_{FA} = 10^{-2} M$ ;  $[Cl^-] = 10^{-1} M$ .

where:  $D$  = overall distribution coefficient;  
 $K_{BH}^x, K_B^x$  = ion-exchange selectivity coefficients for the monovalent and bivalent anions, respectively;  
 $K_1, K_2$  = protonation constant of the anions;  
 $[H^+]$  = hydrogen ion concentration (mequiv./ml);  
 $[Cl^-]$  = chloride ion concentration (mequiv./ml);  
 $Q$  = resin capacity (mequiv./g).

The values of the ion-exchange selectivity coefficients were calculated using the above equation by an Algol computer program based on the principles of least squares. Details of the computation and the program have been described elsewhere<sup>5</sup>.

The calculated ion-exchange selectivity coefficients for the monovalent and bivalent anions of maleic and fumaric acids are given in Table I.

TABLE I

ION-EXCHANGE SELECTIVITY COEFFICIENTS FOR THE MONOVALENT AND BIVALENT ANIONS OF MALEIC AND FUMARIC ACIDS AND THE LOGARITHM OF THE PROTONATION CONSTANTS<sup>6</sup> OF THE ANIONS AT ROOM TEMPERATURE

Compound	$K_{BH}^x$	$K_B^x$	Log $K_1$	Log $K_2$
Maleic acid	2.96	0.022	5.90	1.80
Fumaric acid	1.70	0.063	4.39	3.02

From a comparison of the selectivity coefficients, it can be seen that the selectivity increases in the following order:  $M^{2-} < F^{2-} < FH^- < MH^-$ . This selectivity series follows the decreasing order of the protonation constants of the anions. This observation can be explained by the specific ion hydration effect, discussed by Chu *et al.*<sup>7</sup> The value of the protonation constant is a measure of the base strength of the anion. A strong base has a strong interaction with water and is strongly hydrated, while a weak base has a weak interaction with water and is less hydrated. Hence it would be expected that the strong base would prefer the aqueous phase rather than the exchanger phase, while the weak base is preferentially adsorbed by the resin.

In the resin phase, the degree of hydration of the monovalent and bivalent anions was studied by NMR spectrometry and typical NMR spectra are shown in Fig. 2.

An aqueous suspension of the resin gives a well defined NMR spectrum exhibiting two peaks corresponding to the protons of water inside and outside the resin particles. The ion shift, relative to the peak of the outside water, can be explained in terms of structure-breaking and structure-making effects of the ions on the bulk solvent. Breaking of the hydrogen bonds by ions results in an upfield shift of the peak, while polarization of the water molecules by ions results in a downfield shift of the peak. The value of the shift, as pointed out by Reichenberg and Lawrenson<sup>8</sup>, is determined by the swelling of the resin. The shift is largest when the swelling is low.

The spectra in Fig. 2 indicate that the shift is negative (downfield shift) and is large when the resin is in the monovalent ionic form. These ions are less well hydrated and are preferentially adsorbed. The two peaks appear, however, when the resin is converted into the bivalent ionic form, such ions being more hydrated and less preferentially adsorbed by the resin.

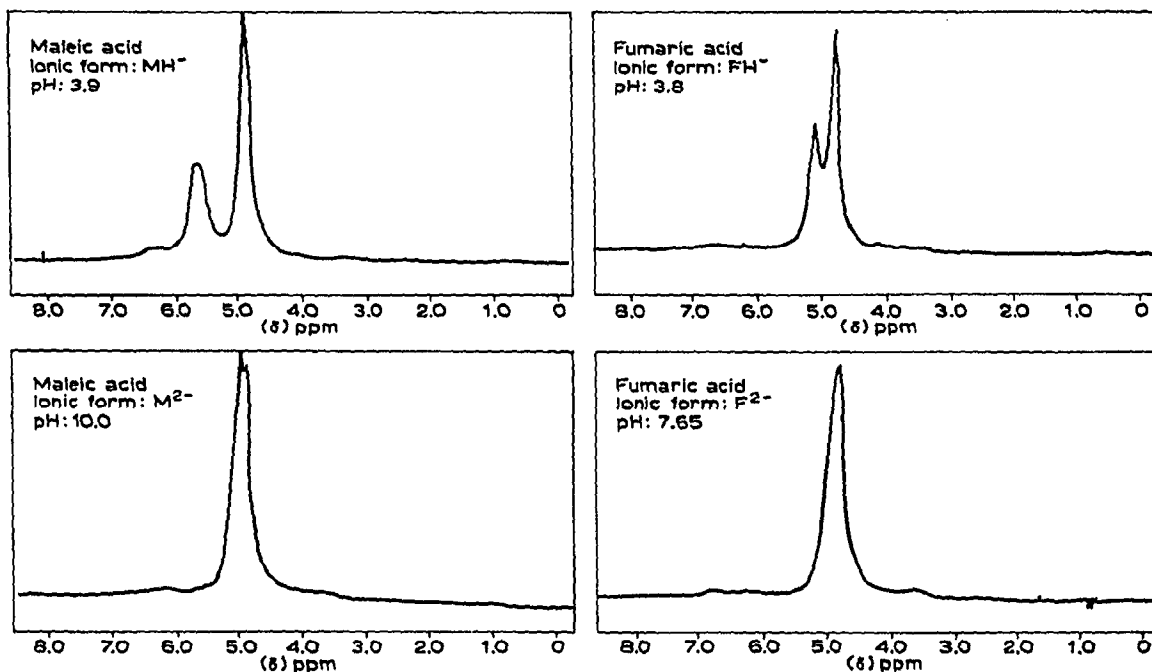


Fig. 2. NMR spectra of the aqueous resin suspension. Resin: Dowex 1-X8 (100–200 mesh). Resin: water ratio = 1:1.

#### ACKNOWLEDGEMENT

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#### REFERENCES

- 1 P. Jandera and J. Churáček, *J. Chromatogr.*, 86 (1973) 351.
- 2 J. Inczédy, *Analytical Applications of Ion Exchangers*, Pergamon Press, Oxford, 1964.
- 3 P. J. Elving and J. Rosenthal, *Anal. Chem.*, 26 (1954) 1454.
- 4 J. Inczédy and L. Glósz, *Acta Chim. Acad. Sci. Hung.*, 62 (1969) 241.
- 5 A. Marton and J. Inczédy, *Magy. Kém. Foly.*, 80 (1974) 145.
- 6 J. Inczédy, *Komplex egyensúlyok analitikai alkalmazása*, Műszaki Könyvkiadó, Budapest, 1970.
- 7 B. Chu, D. C. Whitney and R. M. Diamond, *J. Inorg. Nucl. Chem.*, 24 (1962) 1405.
- 8 D. Reichenberg and I. J. Lawrenson, *Trans. Faraday Soc.*, 59 (1963) 141.