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## EFFECT OF COMPLEX FORMATION IN THE SEPARATION OF SOME PHENOLS BY ION-EXCHANGE CHROMATOGRAPHY

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### SUMMARY

The separation of mixtures of simple phenols in aqueous acid solution has been studied by ion-exchange chromatography; Dowex 50W-X8, a strongly acid cation-exchange resin, was used in the separation. This exchanger, in its H<sup>+</sup> form, shows no affinity for phenols in acid solution, but in Fe<sup>3+</sup> form it shows considerable affinity for phenols. This is attributed to complex formation between the resin and the phenols. Chromatographic separation of four phenols was achieved by elution from a column of the Dowex resin in Fe<sup>3+</sup> form.

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### INTRODUCTION

It has been shown<sup>1–3</sup> that phenol and its simple derivatives form weak complexes with metals (metal-to-ligand ratio 1:1) within the pH range 1.0–2.8. The formation of the phenol–Fe(III) complex is preceded by intermolecular proton transfer, *viz.* [Fe(H<sub>2</sub>O)<sub>4</sub>(OH)(HOC<sub>6</sub>H<sub>4</sub>X)]<sup>2+</sup>; this mechanism was confirmed for mono-, di- and tri-substituted phenols having p*K*<sub>a</sub> values < 3.

The stability of this complex has been shown<sup>3</sup> to depend substantially on the pH of the solution, and the types and positions of the substituents in the aromatic ring. These properties suggest that different phenols have different affinities for the ion-exchange resin and that different separations would be possible in the column.

The flow-rate and theoretical plate height were calculated on the basis of the rate theory. According to the rate theory of Glueckauf<sup>4</sup>, the optimum flow-rate (*v*) of solution through a column can be expressed as:

$$v = \frac{3.38 (D_1 + \beta)^2 D}{0.266 (D_1) r_0} \quad (1)$$

where *D*<sub>1</sub> is the column-distribution coefficient, *β* is the fractional void volume of the bed, *D* is the diffusion coefficient of the compounds under test in the interstitial liquid and *r*<sub>0</sub> is the particle radius.

The theoretical plate height ( $H$ ) was calculated from the following relationship<sup>4</sup>:

$$H = 1.64r_0 + \frac{D_1}{(D_1 + \beta)^2} \frac{0.14r_0v}{\bar{D}} + \frac{D_1}{(D_1 + \beta)} \frac{0.266vr_0}{D(1 + 70r_0v)} + \frac{D\sqrt{2\beta}}{v} \quad (2)$$

where  $\bar{D}$  is the diffusion coefficient of the compounds investigated in the ion-exchange phase.

## EXPERIMENTAL

### Reagents and solvents

The following analytical-grade reagents were used:  $\text{Fe}(\text{NO}_3)_3$ ,  $\text{HClO}_4$ ,  $\text{NaClO}_4$ , *m*-chloro-, *m*-bromo- and *m*-nitrophenol and *m*-cresol (BDH, Poole, Great Britain) and Dowex 50W-X8 resin (150–200 mesh) (Dow Chemical Co., Midland, MI, U.S.A.). De-ionised water (specific conductivity 0.1–0.2  $\mu\text{S}$ ) was used for preparation of solutions. The solution of  $\text{Fe}(\text{ClO}_4)_3$  was prepared by adding 30%  $\text{HClO}_4$  in excess to freshly precipitated and washed  $\text{Fe}(\text{OH})_3$ .

### Apparatus

The experiments were carried out in the apparatus shown diagrammatically in Fig. 1.

The ion-exchange column (1 m  $\times$  15 mm) under thermostatic control was fed with eluent via a piston pump. A sample of volume of 0.5  $\text{cm}^3$  was applied to the top of column with a syringe, and the phenols in the eluate were determined by spectrophotometry in a flow-through quartz 1-cm cell.

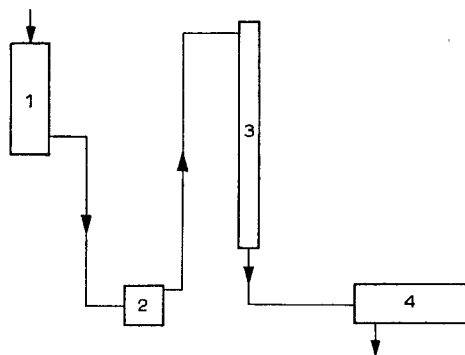


Fig. 1. Schematic diagram of apparatus for separation of simple phenols by ion-exchange chromatography. 1 = Eluent container; 2 = piston pump; 3 = column; 4 = UV spectrophotometer.

### Method

The Dowex 50W-X8 resin was converted into  $\text{Fe}^{3+}$  form under dynamic conditions and then used to fill the prepared glass column. A solution containing the four test phenols ( $10^{-4}$  equiv. of each) was applied to the top of the column, and elution was carried out with a mixture of  $\text{HClO}_4$  and  $\text{NaClO}_4$  (ionic strength 1.0) at pH 3.0–5.0 as eluent.

The exchange isoplanes of the phenols in the eluate were found by spectrophotometry.

## RESULTS AND DISCUSSION

The optimum parameters for separation of the phenols were calculated, using the values ( $D_1$ ,  $\bar{D}$ ,  $D$ ) found in static studies<sup>3</sup>; these parameters are summarised in Table I.

The resulting elution curves are shown in Fig. 2a. For comparison, Fig. 2b shows the elution curve obtained under the same hydrodynamic conditions with the resin in  $H^+$  form.

TABLE I

CALCULATED PARAMETERS FOR SEPARATION OF SIMPLE PHENOLS AT 300°K  
Values relate to a column of Dowex 50W-X8 resin ( $Fe_3^+$ ), 150–200 mesh.

Phenol	Flow-rate (cm/sec)	Number of Plate theoretical height plates (mm)	Bed height (cm)	Bed volume (cm <sup>3</sup> )
<i>m</i> -Cresol	0.063	700	8.0	85.5
<i>m</i> -Nitrophenol	0.041	650	10.0	98.0
<i>m</i> -Bromophenol	0.011	480	12.0	120.0
<i>m</i> -Chlorophenol	0.009	320	16.0	155.0

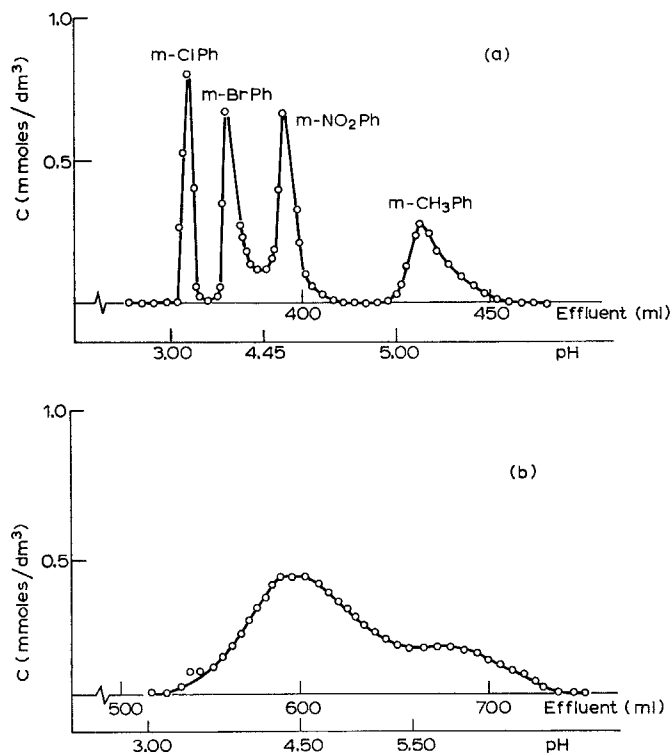
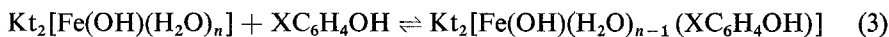


Fig. 2. Elution curves for phenols. Eluent:  $HClO_4$  plus  $NaClO_4$  (ionic strength = 1.00). Temperature, 300°K. Resin: Dowex 50W-X8 (150–200 mesh) in (a)  $Fe_3^+$  form, (b)  $H^+$  form.

The curve in Fig. 2a has distinctly separated bands corresponding to the four phenols; the elution curve for the  $H^+$  form of the resin shows no such bands.

The separation of the phenols by elution can be explained in terms of a considerably increased selectivity of the resin in  $Fe^{3+}$  form compared with that in  $H^+$  form. The stability of the complexes varies with the type of substituent, decreasing in the sequence  $m-CH_3$ ,  $m-NO_2$ ,  $m-Br$ ,  $m-Cl$ .

Because of the complex process of hydrolysis of  $Fe^{III}$ , the complexation reactions in the ion-exchange column might proceed as follows:



where  $n$  has the value 1, 2, 3, 4 or 5 and  $Kt$  represents the strongly acid cation-exchange resin.

Our experiments with model solutions have confirmed the fact that a strongly acid cation-exchange resin in  $Fe^{3+}$  form can be used in the determination of simple phenols in aqueous solution.

#### REFERENCES

- 1 K. Nakamura, T. Tsuchida, A. Yamagishi and M. Fujimoto, *Bull. Chem. Soc. Jap.*, 46 (1973) 456.
- 2 R. H. Milburn, *J. Amer. Chem. Soc.*, 77 (1955) 2064.
- 3 J. Masłowska and W. Piętek, *Acta Univ. Lodz*, (1980) in press.
- 4 E. Glueckauf, *Trans. Faraday Soc.*, 51 (1955) 34.