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ELUTION BEHAVIOUR OF ACIDS IN ION-EXCLUSION CHROMATOGRAPHY USING A CATION-EXCHANGE RESIN

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SUMMARY

A large number of strong and weak acids have been subjected to ion-exclusion chromatography by elution with water on a hydrogen-form cation-exchange resin. The column void volume (V_0) and inner volume (V_i) were determined from a calibration graph obtained by plotting the retention volumes (V_R) against the first dissociation constants (pK_1) of the acids. The distribution coefficients (K_d) of the acids were calculated from the conventional equation for ion-exclusion chromatography: $V_R = V_0 + K_d V_i$. As the K_d values of most acids are between 0 and 1, it is possible to evaluate by gel chromatography the separation mechanism of acids based on the ion-exclusion effect.

INTRODUCTION

Ion-exclusion chromatography (IEC), developed by Wheaton and Bauman[1] and Wheaton[2], can be used for the separation of non-ionic from ionic materials. In the IEC of acids on a hydrogen-form cation-exchange resin, Harlow and Morman[3] reported the retention data for over 50 acids with widely differing structures. They pointed out that the dissociation constant (pK), solubility in water and molecular weight are important factors in the IEC separation of acids. We have discussed the relationship between the first dissociation constants (pK_1) and retention volumes (V_R) of various acids[4]. Strong acids, such as HCl, HNO_3 and H_2SO_4, which are highly ionized, elute quickly with the eluent front. However, weak acids, such as H_3PO_4, H_2SO_3, HF, HCOOH, CH_3COOH and H_2CO_3, elute slowly in proportion to their pK_1 values. It was evident that the retention volumes of the acids depends on their pK_1 values. This suggests that the mechanism of separation of acids on a hydrogen-form cation-exchange resin can be ascribed to the ion-exclusion effect based on the

Donnan membrane equilibrium between the hydrogen ions of the solute and the fixed hydrogen ions of the resin.

The purpose of this work was to evaluate by gel chromatography the separation mechanism of various acids by elution with water on a hydrogen-form cation-exchange resin. The column void volume (V_0) and inner volume (V_t) were determined from exclusion limits and total permeation limits obtained by plotting retention volumes against the pK_1 values of 22 acids. Further, the value of V_t was also determined by gravimetry[5] and compared with that obtained by IEC. The distribution coefficients (K_d) of the acids were calculated from the conventional equation for IEC:

$$V_R = V_0 + K_d V_t \tag{1}$$

This equation is the same as the equation for gel chromatography based on the steric exclusion effect[5].

EXPERIMENTAL

The apparatus was a Hitachi 034 liquid chromatograph equipped with a Hitachi 030 flow coulometric detector, a Yanagimoto C-202 conductometric detector, a Spectra-Physics 770 spectrophotometric detector or a Hitachi 230 fluorometric detector. Most of acids were monitored with flow coulometric and conductometric detectors. Methanol was monitored by UV absorption at 190 nm and phenol by UV absorption at 245 nm and fluorescence at 300 nm. As the chromatograms of H_2S and HCN obtained with the flow coulometric and conductometric detectors showed complex patterns, the effluent fractions were identified by the lead acetate method for H_2S and by the pyridine–pyrazolone method for HCN. A hydrogen-form cation-exchange resin, Hitachi 2613 (particle size 18 ± 2 μm, degree of cross-linking 8%), was packed into a glass-jacketted column (535×9 mm I.D.) by the slurry packing technique. The column was thermostatted at $50°$. De-ionized water was used as the eluent and the flow-rate was 1 ml/min.

All stock solutions of acids were prepared by dissolving the free acids or the corresponding alkali metal salts (reagent grade) in de-ionized water. Sample solutions (100 mg/l) were introduced into the column with a 0.5-ml loop injector.

Chromatograms were recorded with a strip-chart recorder (National VP-6541A), and the retention times and peak areas were registered with a digital integrator (Takeda-riken TR-2213).

RESULTS AND DISCUSSION

Retention volumes of acids

Table I gives the retention volumes of 22 different acids obtained by using water as the eluent. Strong acids such as HI, HBr, HCl, H_2SO_4 and HNO_3, which are highly ionized, were eluted at 12.8 ml. Weak acids such as $(COOH)_2$, H_3PO_3, H_3PO_2, H_3PO_4, H_2SO_3, HF, HCOOH, CH_3COOH and C_2H_5COOH, which are incompletely ionized, were eluted more slowly than the strong acids. Very weak acids such as H_2CO_3, HCN, H_3BO_3, phenol and methanol, which are almost unionized, were eluted at about 28.5 ml. However, C_3H_7COOH and H_2S were eluted at 30.0

TABLE I

RETENTION VOLUMES (V_R) OF ACIDS

Acid	Compound used	V_R (ml)	Acid	Compound used	V_R (ml)
HI	KI	12.8			
HBr	KBr	12.8	HF	NaF	18.4
$HClO_4$	$HClO_4$	12.8	HCOOH	HCOOH	19.5
HCl	HCl, KCl	12.8	CH_3COOH	CH_3COOH, CH_3COONa	23.0
H_2SO_4	H_2SO_4, Na_2SO_4	12.8	C_2H_5COOH	C_2H_5COOH	25.5
HNO_3	HNO_3, KNO_3	12.8	C_3H_7COOH	C_3H_7COOH	30.0
			H_2CO_3	Na_2CO_3	28.5
$C(OOH)_2$	$(COONa)_2$	13.0	HCN	KCN	28.5
H_3PO_3	$NaHPO_3$	13.8	H_3BO_3	H_3BO_3	28.5
H_3PO_2	NaH_2PO_2	14.0	C_6H_5OH	C_6H_5OH	28.2
H_3PO_4	H_3PO_4, Na_2HPO_4	14.2	CH_3OH	CH_3OH	28.8
H_2SO_3	Na_2SO_3	14.5	H_2S	Na_2S	34.8

and 34.8 ml, respectively. From these results, it was concluded that the retention volumes of the acids are dependent on their acidities.

Relationship between retention volume and pK_1

The relationship between the retention volumes and the pK_1 values of the acids was investigated in order to elucidate the separation mechanism of the acids. When the retention volumes were plotted against pK_1 (25°), a calibration graph was obtained as shown in Fig. 1. It can be seen that the retention volumes (12.8 ml) of the strong acids, which are completely ionized, were independent of $pK_1(-11$ to $-1.6)$. This shows that the strong acids were completely ion-excluded by the fixed hydrogen ions of the hydrogen-form cation-exchange resin. The retention volumes of the weak acids increased proportionately to the increase in pK_1 ,which shows that the weak acids are not completely ion-excluded by the fixed hydrogen ions of the resin, that
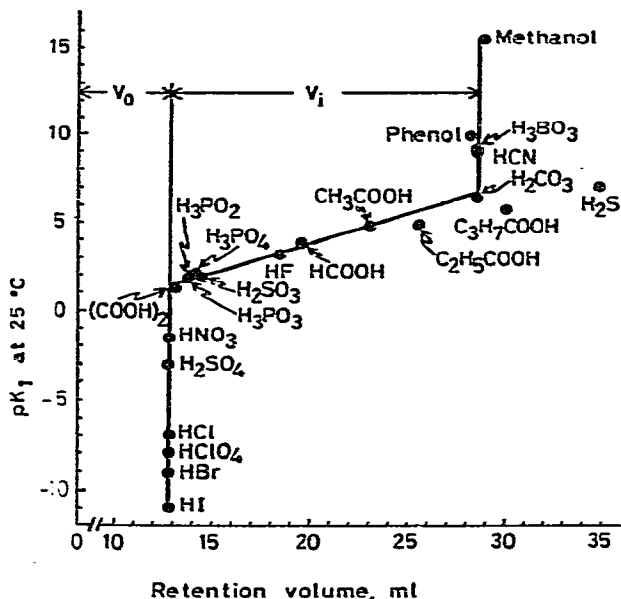

Fig. . Relationship between retention volumes (V_R) and first dissociation constants (pK_1) of acids.

is, the weak acids permeated selectively into the resin. The selective permeation was correlated with the pK_1 values (1.3 to 6.4). The retention volumes (28.5 ml) of the very weak acids were independent of pK_1 (6.4 to 15.5), owing to the total permeation of the very weak acids into the resin.

From Fig. 1, the retention volume (12.8 ml) of the strong acids corresponds to V_0 in eqn. 1. The difference between the retention volumes of the strong acids and the very weak acids corresponds to V_i (15.7 ml). As mentioned above, the values of V_0 and V_i could be determined from the relationship between the retention volumes and the pK_1 values of various acids.

The retention volumes of H_2S, C_2H_5COOH and C_3H_7COOH deviated from the calibration graph, as shown in Fig. 1. It is considered that this behaviour is due to the adsorption effect rather than the ion-exclusion effect between the solute and the resin. In fact, the chromatography of homologous fatty acids, especially hydrophobic fatty acids, on a hydrogen-form cation-exchange resin using water as the eluent has been explained in terms of adsorption chromatography[6,7].

Determination of V_i by gravimetry

In order to establish the validity of the value of V_i obtained by the IEC procedure, V_i was determined by gravimetry. V_i can be calculated from the equation[5]

$$V_i = (W - W_t - W_r - \varrho V_0)/\varrho \tag{2}$$

where W is the total column weight, W_t the unpacked column weight, W_r the dry resin weight and ϱ the density of water. A constant value of W_r was obtained by shrinking the resin by vacuum-drying at 80° for 8 h. The value of V_0 used was the same as that obtained by the IEC procedure. The value of V_i calculated from eqn. 2 was 15.5 ml (average of two determinations), compared with 15.7 ml obtained by the IEC procedure. The agreement between the V_i values was therefore good.

K_d of acids

The K_d value of each acid was determined by substituting the retention volume of each acid as given in Table I and the values of V_0 and V_i obtained by the IEC procedure into eqn. 1.

TABLE II

DISTRIBUTION COEFFICIENTS (K_d) OF ACIDS

Acid	K_d	Acid	K_d
HI	0	HF	0.36
HBr	0	HCOOH	0.43
HClO$_4$	0	CH$_3$COOH	0.65
HCl	0	C$_2$H$_5$COOH	0.81
H$_2$SO$_4$	0	C$_3$H$_7$COOH	1.10
HNO$_3$	0	H$_2$CO$_3$	1.00
(COOH)$_2$	0.01	HCN	1.00
H$_3$PO$_3$	0.06	H$_3$BO$_3$	1.00
H$_3$PO$_2$	0.08	C$_6$H$_5$OH	0.98
H$_3$PO$_4$	0.09	CH$_3$OH	1.02
H$_2$SO$_3$	0.11	H$_2$S	1.40

Table II gives the K_d values of the acids. The K_d values were 0 for the strong acids, 0.01–0.65 for weak acids (except C_2H_5COOH and C_3H_7COOH) and almost 1 for very weak acids (except H_2S). The K_d values of $(COOH)_2$ to H_2CO_3 depended on their pK_1 values. As the K_d values of most acids except H_2S and C_3H_7COOH were between 0 and 1, the mechanism of the separation of acids in IEC on a hydrogen-form cation-exchange resin could be evaluated on the basis of the ion-exclusion effect between the hydrogen ions of solute and the fixed hydrogen ions of the resin.

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