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LIQUID CHROMATOGRAPHY

IV. EFFECTS OF SOLVENT VELOCITY ON SEPARATION USING ION-EXCHANGE RESIN*

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SUMMARY

The classical VAN DEEMTER equation has been modified for use in modern high-pressure liquid chromatography. A number of workers have shown that $H = v^n$ accurately describes many separations in liquid–liquid, liquid–solid, and gel permeation chromatography, where $0.2 \leq n \leq 0.6$. The high-pressure ion-exchange separations of the heavy rare earth ions appears to also be described by the exponential equation over a wide range of flow velocities and under a number of different experimental conditions. In this work $n = 0.145 \pm 0.037$ for flow velocities of 0.057–3.77 cm/sec.

INTRODUCTION

Historically the VAN DEEMTER[1–5] equation has been used to describe the mechanism of liquid chromatographic separations:

$$H = A + B/v + Cv \tag{1}$$

In the last few years, however, a number of workers have found that this equation did not fully describe their experimental observations. SYNDER[6] found that in a system where only the eluent velocity is varied, a more accurate expression is:

$$H = Dv^{0.4} \tag{2}$$

where D is a constant for a given column and set of experimental conditions. WATERS *et al.*[7] were able to show that the exponent was not a constant, but ranged from 0.2

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to 0.6 for a number of different separations. There was no apparent reason the exponent could not assume any value from 0.0 to 1.0, and, in general,

$$H = Dv^n \tag{3}$$

for $0.0 < n < 1.0$.

Because most of the work on column efficiencies and parameters effects involved studies of organic species using analytical columns and submilligram amounts of material, we wondered if the same behavior would be observed in high-speed liquid chromatographic separations of rare earth ions using ion-exchange chromatography. We present the results of our studies herein.

EXPERIMENTAL

A description of the experimental equipment and technique has been published[8,9] and was not further modified for this work. All of the studies reported in this work used AG 50W-X12 ion-exchange resin prepared as previously described. The glass columns were 0.63 and 0.90 cm I.D. and 24.0 and 12.4 cm in length.

For this study it was necessary to hold the separability of adjacent species constant during passage down the column. A solvent gradient, therefore, could not be employed. In order to obtain separations in acceptable periods of time, only the three heaviest rare earths, Lu, Yb, and Tm, were used. Column loads represented at least 15 mg of total rare earth mass and in several cases ranged up to 20 mg of total mass.

An electrical conductivity cell was used to detect the separated species.

RESULTS

We were able to pump from 0.1 to 6.6 ml/min through the columns. Using 0.63 and 0.90-cm diameter columns, this represents a linear flow velocity of 0.057–3.77

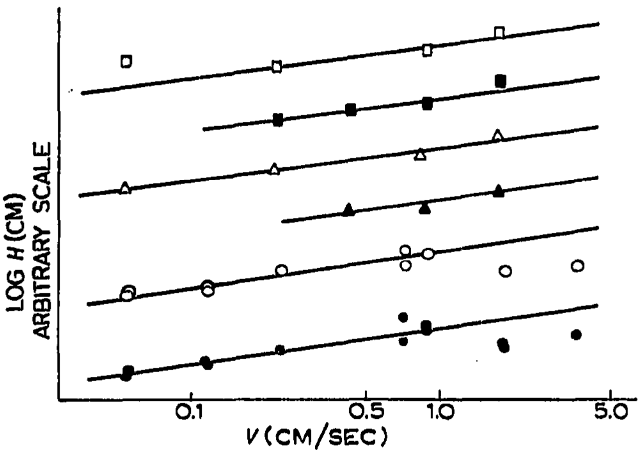

Fig. 1. Plate height (H) *vs.* flow velocity (v) for Lu–Yb and Yb–Tm. ○—○, Lu–Yb, column size 0.63 × 24.0 cm; ●—●, Yb–Tm, column 0.63 × 24.0 cm; △—△, Lu–Yb, column 0.90 × 12.4 cm; ▲—▲, Yb–Tm, column 0.90 × 12.4 cm; □—□, Lu–Yb column 0.90 × 24.8 cm; ■—■, Yb–Tm, column 0.90 × 24.8 cm.

TABLE I

SNYDER PARAMETER AS A FUNCTION OF SOLVENT VELOCITY AND EXPERIMENTAL CONDITION
$\alpha = 1.46 \pm 0.04$ for Lu–Yb and $\alpha = 1.58 \pm 0.05$ for Yb–Tm.

v (*cm/sec*)	*Column diam. × length* (*cm*)	*Lu–Yb*		*Yb–Tm*	
		D	*n*	*D*	*n*
0.0571–3.77	0.63 × 24.0	1.94	0.115 ± 0.063	1.13	0.138 ± 0.051
0.230 –1.85	0.90 × 12.4	0.92	0.204 ± 0.030	0.53	0.140 ± 0.071
0.0588–1.85	0.90 × 24.8	1.24	0.108 ± 0.034	0.68	0.165 ± 0.030
			$\bar{n} = 0.145 \pm 0.037$		

cm/sec and 0.230–1.85 cm/sec, respectively. SNYDER[6] assumed that at very low ($<$ 0.1 cm/sec) and very high ($<$ 10 cm/sec) velocities, eqn. 3 would not apply. As shown in Fig. 1, eqn. 3 appears to be an accurate description of our experimental data for a number of different experimental conditions and over a wide range of flow velocities, including very slow flow of 0.057 cm/sec. The parameters D and n are given in Table I.

Resolution has been defined as the product of a separability factor and a column efficiency factor[10]:

$$R = SQ \tag{4}$$

where

$$Q = V_{oa}/w \tag{5}$$

and

$$S = (\alpha - 1)\left(\frac{K_A}{K_A + 1}\right) \tag{6}$$

It is assumed that the separability factor does not change for a given solvent–solute system as the flow-rate is changed. The values of R, S, and Q for a number of different flow-rates are shown in Table II.

We know column efficiency decreases as plate height, H, increases and a simple relationship is expected between H and the column efficiency factor, Q. Using eqns. 3–6 and an alternative definition of R and H:

TABLE II

RESOLUTION, SEPARABILITY FACTOR, AND COLUMN EFFICIENCY AS A FUNCTION OF SOLVENT VELOCITY

v (*cm/sec*)	*Lu–Yb*			*Yb–Tm*		
	R	*S*	*Q*	*R*	*S*	*Q*
0.0571	1.04	0.400	2.60	1.65	0.381	4.33
0.120	1.01	0.398	2.54	1.56	0.387	4.03
0.234	0.92	0.414	2.22	1.44	0.399	3.61
0.469	0.82	0.384	2.14	1.21	0.393	3.08
0.914	0.84	0.403	2.09	1.28	0.393	3.26
1.89	0.93	0.402	2.31	1.42	0.399	3.56
		$\bar{S} = 0.400 \pm 0.019$			$\bar{S} = 0.392 \pm 0.017$	

$$R = \tfrac{1}{4}\,\frac{\alpha - 1}{\alpha}\,\frac{K_A}{K_A + 1}\,N^{\frac{1}{2}} \tag{7}$$

$$H = L/N \tag{8}$$

It can be shown that

$$H = EQ^{-2} \tag{9}$$

and

$$Q^{-2} = \frac{D}{E}\,v^{n} \tag{10}$$

A plot of Q *vs.* v will have a slope of $-n/2$ as shown in Fig. 2.

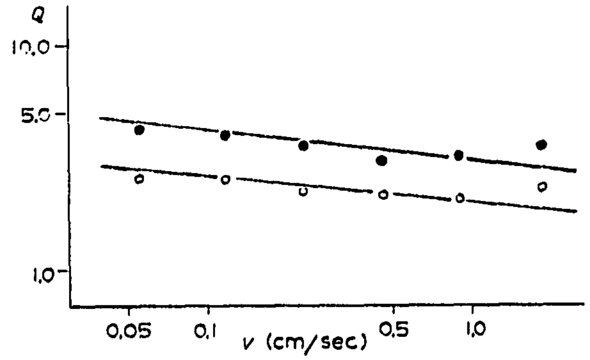

Fig. 2. Column efficiency (Q) *vs.* flow velocity (v) for Lu–Yb (○—○) and Yb–Tm (●—●); column 0.63 × 24.0 cm.

CONCLUSIONS

The mathematical model for chromatographic separation mechanism presented by SNYDER (eqn. 3) appears to describe accurately the high-speed liquid chromatographic separation of mass quantities of rare earths using ion-exchange resin. Eqn. 3 appears valid for flow velocities as low as 0.057 cm/sec in our experiments.

The factor D was a constant for a given column and set of experimental conditions, however, we were not able to relate the constant directly to particle diameter as proposed by SNYDER. The exponential factor, n, as determined from data on 28 experimental separations is 0.145 ± 0.037.

Although plate height and column efficiency are simply related, we find that a plot of Q *vs.* v makes the functional dependence of column efficiency with increasing flow velocity more apparent than the traditional H *vs.* v plot.

As pointed out by WATERS[7], optimization in liquid chromatography involves obtaining the largest possible separation factor with the smallest velocity exponent (n). It has generally been easier to improve the separation factor by developing new packing materials, rather than resorting to extreme pressures to accomplish a resolution of components. In the separation of mass amounts of inorganic species, we did not have a selection of resin materials available and it was, therefore, very fortunate that in all systems we have studied to date the exponential factor is quite small (< 0.2). We have been able to decrease the time required for separation by a factor of ten while only increasing the pressure from a gravity flow to 250 p.s.i.

NOMENCLATURE

A, B, C	Van Deemter equation constants
D	Snyder equation constant—function of column size, packing, particle size, and experimental conditions
E	proportionality constant relating H and Q
H	plate height
K_A	distribution coefficient for component A
L	column length
N	number of theoretical plates
n	exponential factor in Snyder equation
Q	column efficiency factor
R	resolution
S	separability factor
V_{oa}	volume from injection to peak a
v	solvent velocity in a column
w	peak width at base line
α	separation ratio.

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