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EFFECT OF RESIN CROSS-LINKING ON THE ANION-EXCHANGE SEPARATION OF RARE EARTH-EDTA COMPLEXES

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SUMMARY

The anion-exchange separation of rare earth complexes with EDTA on Dowex 1 resins with 2, 4, 8, 10, and 16 nominal cross-linking, respectively, was investigated with loads at tracer levels. Selectivity coefficients, separation factors, plate heights, and resolutions for adjacent peaks were calculated from the elution curves. Although the separation factors increased rather uniformly with the increase in resin cross-linking, the best separations were obtained with Dowex 1 X4 due to the most promising value of the plate height. Plate height, which was the lowest for the X4 resin, was found to increase both with increase and decrease of resin cross-linking. A change from an X4 to an X16 resin resulted in a drastic increase of plate height of nearly two orders of magnitude. It was shown that the results obtained cannot be interpreted on the grounds of the classical GLUECKAUF equation. The introduction of a new term, accounting for longitudinal diffusion in the resin phase, into GLUECKAUF's equation was suggested and the qualitative agreement between theoretical prediction and experimental data was demonstrated.

The existence of a sieve effect in the case of the anion exchange of rare earth-EDTA complexes on highly cross-linked resins was also pointed out.

INTRODUCTION

The effect of resin cross-linking on ion-exchange separations has not been investigated in detail. It is generally assumed in the literature^{1,2} that an increase in cross-linking results in a rise of resin selectivity (as expressed in terms of selectivity coefficient), especially at tracer level loadings. The quality of a separation of two elements under investigation depends, however, on the value of the separation factor (ratio of distribution coefficients) rather than on the absolute values of the selectivity coefficients. Although an increase in the separation factor with an increase of resin cross-linking was observed in many cases³⁻⁹, a survey of other data¹⁰⁻¹² shows that this situation is by no means universal. Furthermore, the quality of separation depends on the dynamics of the column process, which should also change with the change in resin cross-linking. In an attempt to gather more experimental data in order to make some generalizations possible the effect of resin cross-

linking on the separation of several elements in various systems was investigated. In this paper, the first of a series, the results of the separation of rare earth complexes with EDTA on strongly basic anion-exchange resins are presented.

EXPERIMENTAL

Resins

Dowex 1 resins with quaternary ammonium functional groups were employed. Methods of grinding, fractionating and conditioning the resins, as well as microscopic determination of particle size, have been described earlier^{13,14}.

The exchange capacity of strongly basic groups (Z_s) was determined by converting a known amount of resin first to the $[\text{OH}^-]$ -form with 1 *N* NaOH and then to the $[\text{Cl}^-]$ -form with an excess of 1 *N* NaCl solution. After washing the column with deionized water until free from chlorides, Cl^- ions were eluted with 1 *N* NaOH solution and determined titrimetrically¹⁵.

The total exchange capacity (Z_a) was determined in a similar manner except that the resin was converted to the $[\text{Cl}^-]$ -form with 1 *N* HCl solution and the column was washed with absolute ethanol instead of water¹⁶.

To determine the exchange capacity of the resins in ethylenediaminetetraacetate ($[\text{H}_2\text{Y}^{2-}]$)-form, the resin ($[\text{Cl}^-]$ -form) was converted into the $[\text{H}_2\text{Y}^{2-}]$ -form with a large excess of 0.2 *M* $\text{Na}_2\text{H}_2\text{Y}$ solution until no chlorides could be detected in the effluent. After washing with deionized water, H_2Y^{2-} ions were displaced from the resin with 1 *M* NaCl solution and determined by titration with a standard solution of magnesium chloride in the presence of Eriochrome Black T. All the values of exchange capacity were expressed in terms of a number of mequiv./1 g of dry (dried at 105° to a constant weight) resin in a specified ionic form.

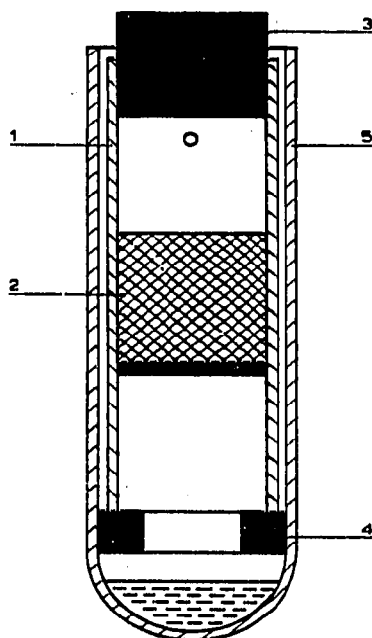


Fig. 1. A device for the determination of the water content of the resin by centrifugation. 1 = Glass tube with a sintered glass disc (G4) in the middle; 2 = ion-exchange resin bed; 3 = rubber bung; 4 = rubber collar; 5 = plastic centrifuge tube.

The water contents of swollen resins were determined by a modified method of PEPPER *et al.*¹⁷. Approximately 4–5 g of water swollen resin ($0.10 \text{ mm} \leq \varnothing \leq 0.30 \text{ mm}$) was placed in a glass vessel with a fritted glass disc (*cf.* Fig. 1) and centrifuged at 3000 r.p.m. (approx. 900 g) for 15 min. After centrifugation the bottom of the vessel touching the rubber ring was placed in contact with blotting paper to remove water droplets adhering to the glass. The vessel with the resin was then weighed, dried at 105° to constant weight, and weighed again. These data together with the weight of empty vessel enabled the calculation of the percentage of water in a swollen resin and its water content (g H_2O per g of the dry resin). The data were corrected for the residual liquid retained at the interface of the beads. This correction (0.034 g H_2O /ml of the bed) was determined by centrifuging glass beads (60 mesh) under the same conditions as stated above and was in a good agreement with the data published in the literature¹⁸.

The density of the dry resin (d_s) was determined picnometrically using the resin dried at 105° and *n*-heptane as the picnometric fluid¹⁹. The density of the swollen resin (d_j) was determined in a similar manner using fully swollen resin (and water)²⁰, and introducing the correction for the water held at the resin bead interface.

Bed density (d_z) (g of dry resin per ml of the bed) was determined by introducing a known amount of the resin in deionized water into graduated cylinder and measuring the volume occupied by the resin bed after settling.

Radioactive tracers and reagents

The following radioactive tracers were used: ^{140}La ($T_{1/2} = 40.2 \text{ h}$); ^{142}Pr ($T_{1/2} = 19.2 \text{ h}$); ^{147}Pm ($T_{1/2} = 2.6 \text{ y}$); ^{153}Sm ($T_{1/2} = 1.96 \text{ d}$); $^{152,154}\text{Eu}$ ($T_{1/2} = 13\text{--}16 \text{ y}$); ^{160}Tb ($T_{1/2} = 73 \text{ d}$); ^{165}Dy ($T_{1/2} = 2.3 \text{ h}$); ^{166}Ho ($T_{1/2} = 27.3 \text{ h}$); ^{170}Tm ($T_{1/2} = 127 \text{ d}$); ^{177}Lu ($T_{1/2} = 6.8 \text{ d}$); ^{46}Sc ($T_{1/2} = 85 \text{ d}$); ^{90}Y ($T_{1/2} = 65 \text{ h}$); ^{134}Cs ($T_{1/2} = 2.3 \text{ y}$).

^{147}Pm and $^{152,154}\text{Eu}$ were supplied by The Centre for Production and Distribution of Isotopes, Świerk. The other rare earth tracers were prepared by neutron irradiation of the appropriate spectrally pure grade of oxides or nitrates in the Polish reactor EWA. The ^{134}Cs was prepared by irradiation of CsCl of spectral purity followed by purification on an ion-exchange column²¹ to remove ^{32}P and ^{32}S formed as result of the reaction of ^{35}Cl with fast neutrons.

Disodium ethylenediaminetetraacetate was prepared by purification of commercial $\text{Na}_2\text{H}_2\text{Y} \cdot 2\text{H}_2\text{O}$ according to BLAEDEL AND KNIGHT^{21a}. An 0.2 M stock solution of $\text{Na}_2\text{H}_2\text{Y}$ was made and other concentrations were prepared from the stock solution by dilution. The exact concentration was checked in each case by titration with standard magnesium chloride solution in the presence of Eriochrome Black T.

All other reagents were of analytical grade.

Apparatus and procedure

Jacketed glass columns of approximately 2 mm internal diameter were employed. Constant temperature ($\pm 0.2^\circ$) was maintained by passing water from a Höppler ultrathermostat through the jacket of the column.

The solution of radioactive tracers of rare earths in HCl together with a small quantity of ^{134}Cs was evaporated to dryness in a glass crucible, then enough $\text{Na}_2\text{H}_2\text{Y}$ solution to complex all the rare earth ions was added and the solution gently evapo-

TABLE I

FUNDAMENTAL PROPERTIES OF THE RESINS EMPLOYED

Resin	Functional groups	Exchange capacity (mequiv./g dry resin [Cl ⁻])				Density ([Cl ⁻]-form)				Maximum water content		Normality of the resin phase for column (Z _s /W _{H₂O}) studies	Particle size of the fraction used
		Z _s	Z _c	Z ₁ ^a	Z ₂ ^b	d _s	d ₁	d ₂	% H ₂ O	W _{H₂O} (g H ₂ O/g dry resin [Cl ⁻])	W _{H₂O} /Z _s (g H ₂ O/mequiv.)		
Dowex I X2	-N(CH ₃) ₃ ⁺ Cl ⁻	4.08	4.12	4.66	4.71	1.09	1.04	0.166	72.53	2.641	0.645	1.55	6 μ ≤ Ø ≤ 38 μ
Dowex I X4	-N(CH ₃) ₃ ⁺ Cl ⁻	3.92	3.95	4.61	4.70	1.06	1.07	0.253	58.36	1.403	0.357	2.80	11 μ ≤ Ø ≤ 42 μ
Dowex I X8	-N(CH ₃) ₃ ⁺ Cl ⁻	3.24	3.24	4.50	4.68	1.07	1.11	0.413	36.12	0.566	0.175	5.72	17 μ ≤ Ø ≤ 44 μ
Dowex I X10	-N(CH ₃) ₃ ⁺ Cl ⁻	2.83	2.83	4.45	4.67	1.07	1.10	0.436	35.74	0.556	0.195	5.11	17 μ ≤ Ø ≤ 46 μ
Dowex I X16	-N(CH ₃) ₃ ⁺ Cl ⁻	1.96	1.97	4.30	4.63	1.04	1.11	0.448	19.03	0.240	0.122	8.17	20 μ ≤ Ø ≤ 43 μ
Amberlite IRA-400	-N(CH ₃) ₃ ⁺ Cl ⁻	3.70	3.76	—	—	1.02	1.09	0.340	44.30	0.795	0.220	4.55	

^a Calculated by assuming that each aromatic ring originating from styrene carries one functional group.

^b Calculated by assuming that each aromatic ring originating both from styrene and divinylbenzene, respectively, carries one functional group.

rated to dryness. The residue was dissolved in $75 \mu\text{l}$ of the eluant ($\text{Na}_2\text{H}_2\text{Y}$ solution of the proper concentration) and $25 \mu\text{l}$ of this solution was pipetted onto the top of the Dowex 1 column ($[\text{H}_2\text{Y}^{2-}]$ -form). The total rare earth content in the "load" did not exceed 0.3% of the exchange capacity of the resin in the column. The mixture was eluted at a constant flow rate, the effluent being collected in drops on a moving paper band. The drops were then automatically dried under infrared lamps, cut out of the band and counted with a G.M. or scintillation counter. The details of the apparatus and procedure have been described earlier^{13,14}.

RESULTS

Physico-chemical characterization of the resin

The fundamental properties of the resins used in this study are summarized in Table I. The data for Amberlite IRA-400 employed in earlier work^{13,22} are also included.

As can be seen all the resins studied can be regarded as monofunctional. The exchange capacity was found to be considerably lower than that calculated, assuming that each aromatic ring carries one functional group. The differences between the theoretical and experimental values, which are especially notable for resins of higher cross-linking, were considerably greater than those observed for sulfonic acid cation-exchange resins²³.

This evidently reflects the much greater complexity of the production of anion-exchange resins (chloromethylation followed by amination) compared with the sulfonation reaction used to prepare cation exchangers from the same styrene-divinylbenzene copolymer. It is probable that side reactions accompanying the

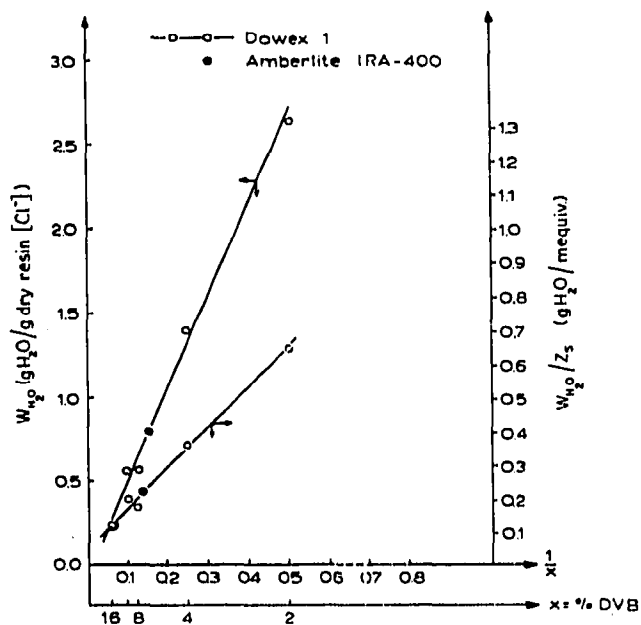


Fig. 2. Water content ($W_{\text{H}_2\text{O}}$) and specific water content ($W_{\text{H}_2\text{O}}/Z_n$) of Dowex 1 resins as a function of the reciprocal of the nominal divinylbenzene content.

chloromethylation and resulting in the formation of additional cross-linkings *via* methylene bridges are to some extent responsible for this effect²⁴.

When attempting to correlate the quality of separation with resin cross-linking it is desirable to express the latter not in terms of "nominal divinylbenzene content" (mole per cent of DVB in the polymerization mixture)¹, which does not necessarily reflect the actual cross-linking in the resin, but in terms of some readily measurable physical property of the exchanger. As can be inferred from Table I, the density of both the dry and swollen ion exchanger is characteristic for the kind of exchanger rather than its cross-linking. On the other hand such properties as bed density, maximum water content and normality of the resin phase change relatively regularly with the increase in cross-linking and can be used for its characterization, as has also been done by other workers^{17,24-27}.

In Fig. 2, the water content (W_{H_2O}) and the specific water content (W_{H_2O}/Z_s), respectively, are plotted *vs.* reciprocal of the nominal DVB content. As can be seen there is almost exactly linear dependence between W_{H_2O} or W_{H_2O}/Z_s and $1/X$ ($X = \% \text{ DVB}$). Slight deviations observed for X8-X10 resins might conceivably stem from some inhomogeneities of the resin phase in these exchangers.

Similar straight-line dependence was obtained on plotting $(V_j/V_s - 1)$ (where V_j and V_s are the equivalent volumes of the swollen and dry resin, respectively) *vs.* $1/X$ according to the method of BOYD AND SOLDANO²⁸.

Basic relationships

Weight distribution coefficients of the rare earths (amount per g of dry resin/amount per ml of solution) were calculated from elution curves by means of the equation²²

$$\lambda_{LnY^-} = \frac{U_{\max.(LnY^-)} - (U_0 + V)}{m_j} = \frac{U_{\max.(LnY^-)} - U_{\max.(Cs^+)}}{m_j} \quad (1)$$

where:

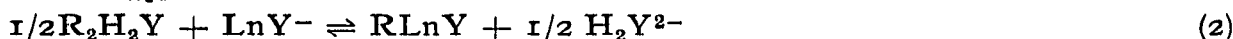
$U_{\max.}$ = volume of the eluant at which the concentration of a given ion reached its maximum (ml)

U_0 = dead volume of the column

V = free volume of the resin bed

m_j = weight of the dry ion-exchange resin in the column (g)

From these data selectivity coefficients, $k_{H_2Y^{2-}}^{LnY^-}$, and "corrected" selectivity coefficients $k'_{H_2Y^{2-}}^{LnY^-}$, for the ion-exchange reaction:



were calculated by the formula^{22,29}

$$k_{H_2Y^{2-}}^{LnY^-} = \frac{\lambda_{LnY^-} \cdot m^{1/2}_{H_2Y^{2-}} \cdot d}{C_r} \quad (3)$$

where

$m_{H_2Y^{2-}}$ = molality of eluant (Na_2H_2Y) solution

d = density of eluant solution

C_r = concentration of the resin phase (mmole per g of dry resin [H_2Y^{2-}])

and

$$k' \frac{\text{LnY}^-}{\text{H}_2\text{Y}^{2-}} = k \frac{\text{LnY}^-}{\text{H}_2\text{Y}^{2-}} \frac{\gamma^{3/2} \text{Na}_2\text{H}_2\text{Y}}{\gamma^2 \text{NaLnY}} \quad (4)$$

where γ denotes the mean activity coefficients which can be derived from the tables published by LIETZKE³⁰. Separation factors of adjacent elements are given by:

$$\alpha_1^2 = \frac{\lambda_{\text{LnY}^- (2)}}{\lambda_{\text{LnY}^- (1)}} \quad (5)$$

In addition plate heights³¹ are given by:

$$H = \frac{L \cdot W^2}{8(U_{\text{max.}} - U_0)^2} = \frac{L \cdot \sigma^2}{(U_{\text{max.}} - U_0)^2} \quad (6)$$

where

L = length of the resin bed

W = width of the peak for the $M = \frac{M_{\text{max.}}}{e} = 0.368 M_{\text{max.}}$ ordinate

$\sigma = \frac{W}{2\sqrt{2}}$ = standard deviation of chromatographic peak.

The resolution³¹ was also calculated from:

$$R_3 = \frac{U_{\text{max.}(2)} - U_{\text{max.}(1)}}{3 \cdot (\sigma_1 + \sigma_2)} \quad (7)$$

Analysis of the separations

Typical elution curves of the rare earth ethylenediaminetetraacetates at 25° and 75° from the five resins employed are presented in Figs. 3-6. In each series the dimensions of the resin bed were nearly identical for all exchangers and the concentrations of the eluant solution were so chosen that the peak elution volumes of one of the middle elements were approximately the same (at 25°).

As the particle size of the resins and the flow rates were also approximately equal, these elution curves are directly comparable. Plate heights, separation factors, and resolutions for adjacent peaks were calculated with the aid of eqns. 6, 5 and 7 respectively and are also listed in the figures.

One can see at once from Figs. 3-6 that the separating ability of the resin depends very much on its cross-linking, the separation being quite unsatisfactory with the highest cross-linkings.

However, the separation factors of the rare earths do even increase (more or less regularly) with a decrease in specific water content, *i.e.* with an increase of resin cross-linking (see Fig. 7). The origin of the changes in the degree of separation must therefore lie elsewhere.

As was pointed out previously, resolution, which is a quantitative measure of separation efficacy, is a function of separation factor and of plate height³¹, *viz.*

$$R_3 = \frac{(\alpha_1^2 - 1) \cdot \sqrt{L}}{3(\alpha_1^2 + 1) \cdot \sqrt{H}} \quad (8)$$

where \bar{H} is the mean plate height.

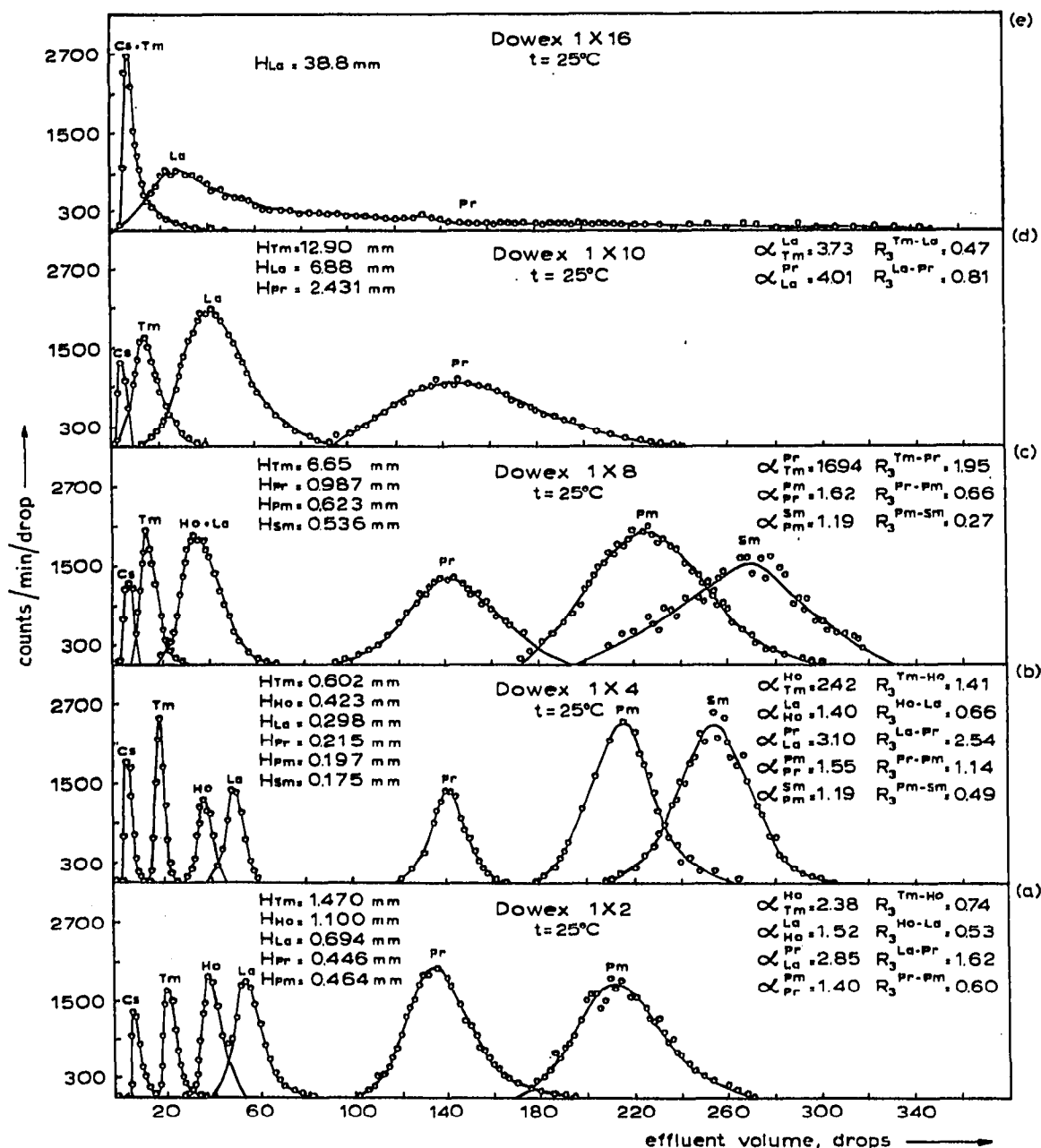


Fig. 3. Effect of resin cross-linking on the separation of Tm, Ho, La, Pr, Pm and Sm ethylenediaminetetraacetates at 25° . (a) Dowex 1 X2 [H_2Y^{2-}] ($6 \mu \leq \varnothing \leq 38 \mu$); column: $5.30 \text{ cm} \times 0.0310 \text{ cm}^2$; eluant: $0.011 \text{ M Na}_2\text{H}_2\text{Y}$; flow rate: 0.91 cm/min . (b) Dowex 1 X4 [H_2Y^{2-}] ($11 \mu \leq \varnothing \leq 42 \mu$); column: $5.30 \text{ cm} \times 0.0310 \text{ cm}^2$; eluant: $0.036 \text{ M Na}_2\text{H}_2\text{Y}$; flow rate: 1.19 cm/min . (c) Dowex 1 X8 [H_2Y^{2-}] ($17 \mu \leq \varnothing \leq 44 \mu$); column: $5.30 \text{ cm} \times 0.0310 \text{ cm}^2$; eluant: $0.078 \text{ M Na}_2\text{H}_2\text{Y}$; flow rate: 1.22 cm/min . (d) Dowex 1 X10 [H_2Y^{2-}] ($17 \mu \leq \varnothing \leq 46 \mu$); column: $5.30 \text{ cm} \times 0.0310 \text{ cm}^2$; eluant: $0.096 \text{ M Na}_2\text{H}_2\text{Y}$; flow rate: 1.17 cm/min . (e) Dowex 1 X16 [H_2Y^{2-}] ($20 \mu \leq \varnothing \leq 46 \mu$); column: $5.30 \text{ cm} \times 0.0310 \text{ cm}^2$; eluant: $0.029 \text{ M Na}_2\text{H}_2\text{Y}$; flow rate: 1.21 cm/min .

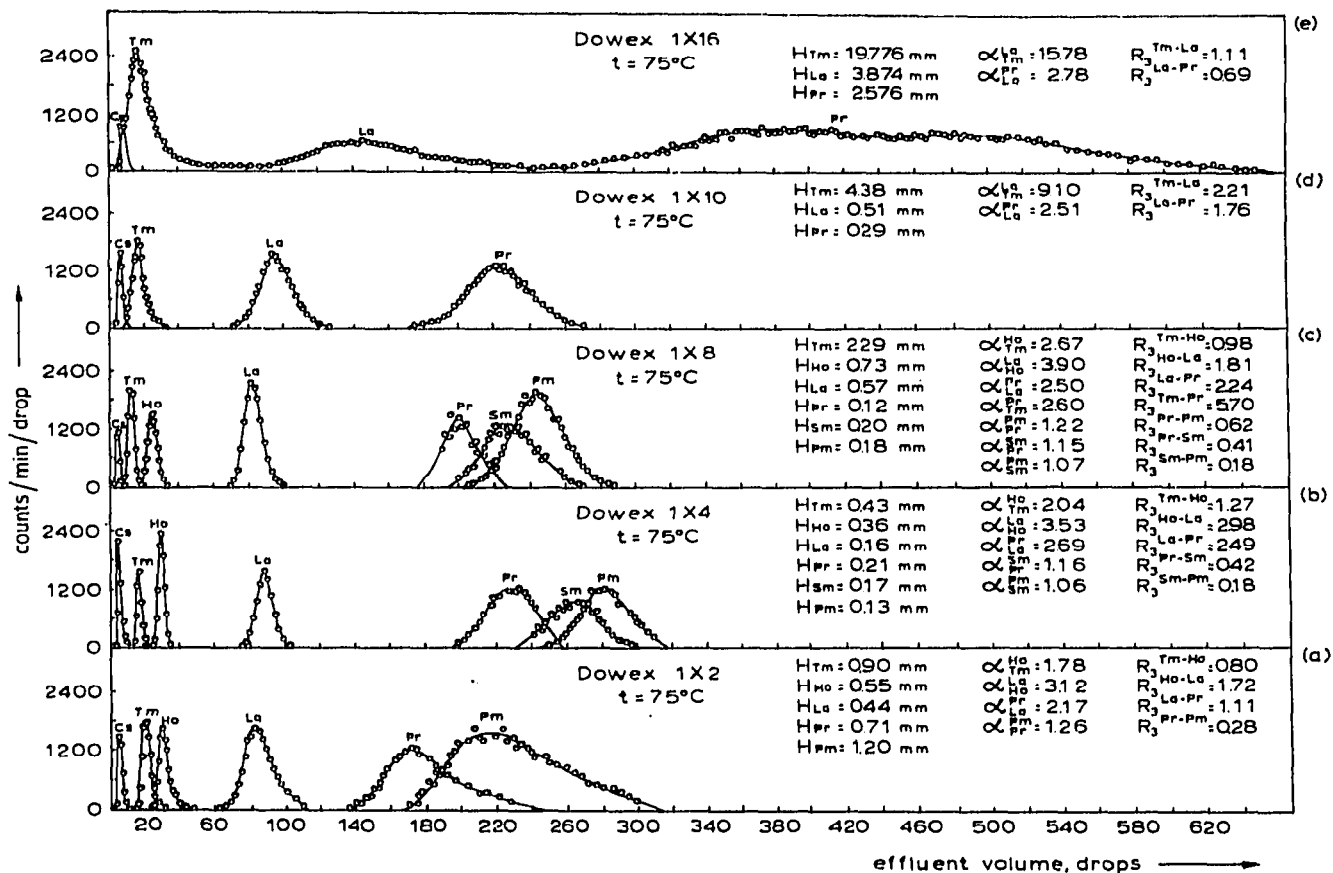


Fig. 4. Effect of resin cross-linking on the separation of Tm, Ho, La, Pr, Pm and Sm ethylenediaminetetraacetates at 75°. (a) Dowex 1X2 [H_2Y^{2-}] ($6 \mu \leq \phi \leq 38 \mu$); column: 5.30 cm \times 0.0310 cm²; eluant: 0.011 M Na₂H₂Y; flow rate: 1.21 cm/min. (b) Dowex 1X4 [H_2Y^{2-}] ($11 \mu \leq \phi \leq 42 \mu$); column: 5.30 cm \times 0.0310 cm²; eluant: 0.036 M Na₂H₂Y; flow rate: 1.12 cm/min. (c) Dowex 1X8 [H_2Y^{2-}] ($17 \mu \leq \phi \leq 44 \mu$); column: 5.30 cm \times 0.0310 cm²; eluant: 0.078 M Na₂H₂Y; flow rate: 1.15 cm/min. (d) Dowex 1X10 [H_2Y^{2-}] ($17 \mu \leq \phi \leq 46 \mu$); column: 5.30 cm \times 0.0310 cm²; eluant: 0.096 M Na₂H₂Y; flow rate: 1.15 cm/min. (e) Dowex 1X16 [H_2Y^{2-}] ($20 \mu \leq \phi \leq 46 \mu$); column: 5.30 cm \times 0.0310 cm²; eluant: 0.029 M Na₂H₂Y; flow rate: 1.16 cm/min.

The theoretical expression for the plate height in ion-exchange chromatography as derived by GLUECKAUF³² and with subsequent refinements^{1,33} is given by:

$$H = 1.64 \cdot r_0 + \frac{\lambda' \cdot 0.142 \cdot r_0^2 \cdot u}{(\lambda' + i)^2 \cdot D} + \frac{(\lambda')^2 \cdot 0.266 \cdot r_0 \cdot u}{(\lambda' + i)^2 (1 - i) \cdot D \cdot (1 + 70r_0 u)} + \frac{D \cdot i \cdot \sqrt{2}}{u} \quad (9)$$

where

r_0 = mean radius of resin particles

D and D = diffusion coefficients in the resin and in solution phases, respectively

λ' = volume distribution coefficient ($\lambda' = \lambda \cdot d_z$)

i = fractional free volume of the resin bed

u = linear flow rate of eluant solution

It follows from this equation that the plate height depends on the distribution coefficient of the eluted species if the particle diffusion mechanism is predominant or at least significant. The plate height should then increase with the increase of $1/(\lambda' + i) \cong 1/\lambda'$.

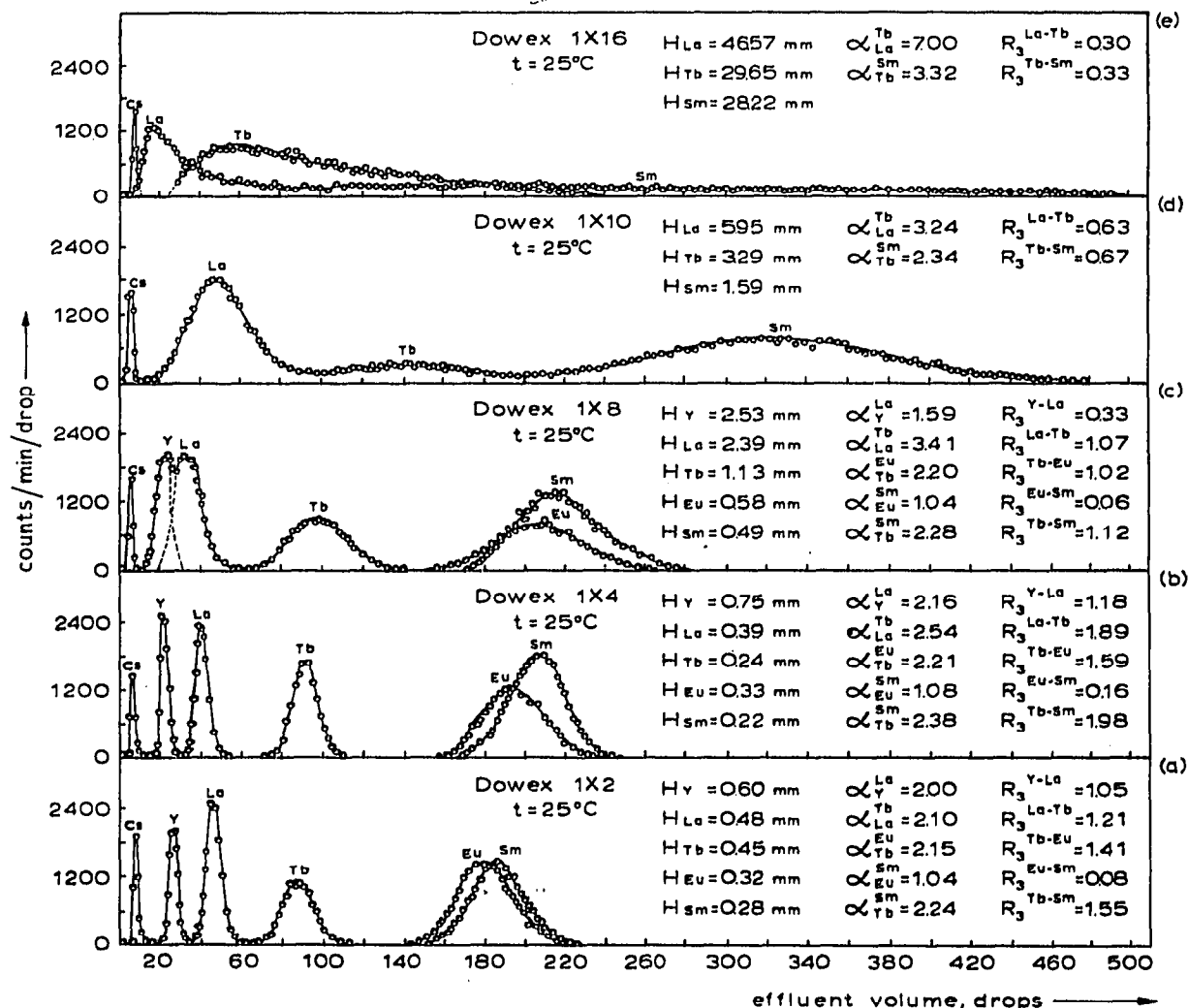


Fig. 5. Effect of resin cross-linking on the separation of Y, La, Tb, Eu and Sm ethylenediaminetetraacetates at 25°. (a) Dowex 1 X2 [H_2Y^{2-}] ($6 \mu \leq \varnothing \leq 38 \mu$); column: 4.90 cm \times 0.0305 cm²; eluant: 0.011 M Na₂H₂Y; flow rate: 0.95 cm/min. (b) Dowex 1 X4 [H_2Y^{2-}] ($11 \mu \leq \varnothing \leq 42 \mu$); column: 4.90 cm \times 0.0305 cm²; eluant: 0.036 M Na₂H₂Y; flow rate: 1.32 cm/min. (c) Dowex 1 X8 [H_2Y^{2-}] ($17 \mu \leq \varnothing \leq 44 \mu$); column: 4.95 cm \times 0.0305 cm²; eluant: 0.078 M Na₂H₂Y; flow rate: 1.33 cm/min. (d) Dowex 1 X10 [H_2Y^{2-}] ($17 \mu \leq \varnothing \leq 46 \mu$); column: 5.10 cm \times 0.0305 cm²; eluant 0.063 M Na₂H₂Y; flow rate: 1.18 cm/min. (e) Dowex 1 X16 [H_2Y^{2-}] ($20 \mu \leq \varnothing \leq 43 \mu$); column: 4.90 cm \times 0.0305 cm²; eluant: 0.048 M Na₂H₂Y; flow rate: 1.31 cm/min.

This is indeed the case when separating rare earth ethylenediaminetetraacetates (see Fig. 8). Therefore comparisons made in order to evaluate the effect of resin cross-linking on plate height should be made not only at constant ν_0 and u but also at constant λ' (which can be read from such a plot as that presented in Fig. 8).

In Fig. 9 the plate height, normalized for the value of a volume distribution coefficient of $\lambda' = 20$, is plotted as a function of specific water content. As can be seen the dependence of H on the cross-linking is unexpectedly great.

The most favourable (the lowest) H value is achieved at relatively low cross-linking ($X = 3-4$). When changing to highly cross-linked resins ($X = 16$), the plate height is increased by more than two orders of magnitude (at 25°). The plate height

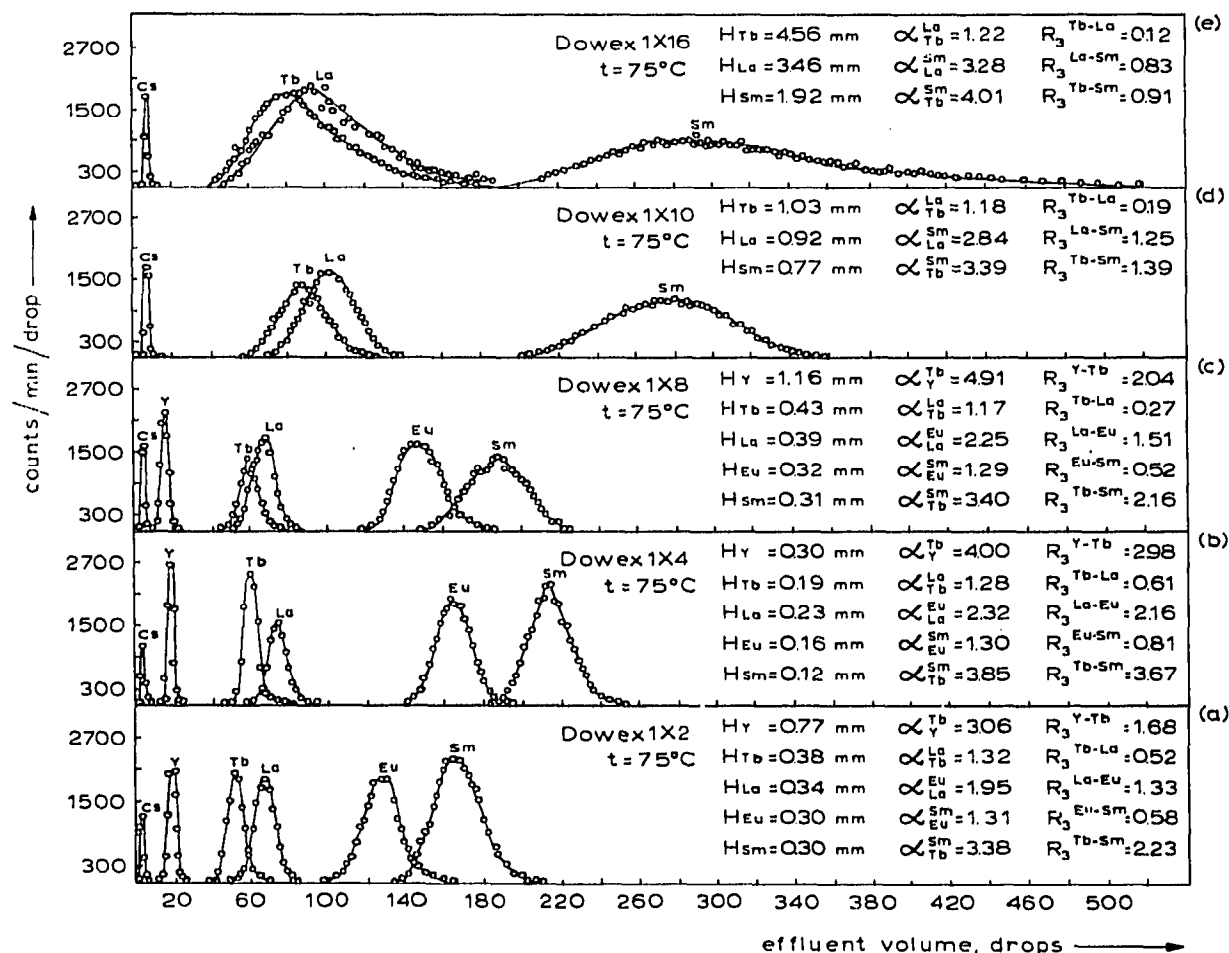


Fig. 6. Effect of resin cross-linking on the separation of Y, La, Tb, Eu and Sm ethylenediaminetetraacetates at 75°. (a) Dowex 1 X2 [H_2Y^{2-}] ($6 \mu \leq \phi \leq 38 \mu$); column: 4.90 cm \times 0.0305 cm²; eluant: 0.011 M Na₂H₂Y; flow rate: 1.18 cm/min. (b) Dowex 1 X4 [H_2Y^{2-}] ($11 \mu \leq \phi \leq 42 \mu$); column: 4.85 cm \times 0.0305 cm²; eluant: 0.036 M Na₂H₂Y; flow rate: 1.26 cm/min. (c) Dowex 1 X8 [H_2Y^{2-}] ($17 \mu \leq \phi \leq 44 \mu$); column: 4.80 cm \times 0.0305 cm²; eluant: 0.078 M Na₂H₂Y; flow rate: 1.29 cm/min. (d) Dowex 1 X10 [H_2Y^{2-}] ($17 \mu \leq \phi \leq 46 \mu$); column: 4.95 cm \times 0.0305 cm²; eluant: 0.063 M Na₂H₂Y; flow rate: 1.23 cm/min. (e) Dowex 1 X16 [H_2Y^{2-}] ($20 \mu \leq \phi \leq 43 \mu$); column: 4.90 cm \times 0.0305 cm²; eluant: 0.048 M Na₂H₂Y; flow rate: 1.33 cm/min.

also increases when going to lower ($X = 2$) cross linkings.

As a corollary, the resolution of rare earth pairs is best with Dowex 1 X4 and decreases with both an increase and decrease of cross-linking (see Fig. 10), despite the other trend in the separation factors (see Fig. 7).

DISCUSSION

As can be seen from Fig. 8 the plate height for Dowex 1 X16 is a linear function of $1/\lambda'$ which indicates that the particle diffusion mechanism (the second term in eqn. 9) is predominant. On going to lower cross-linkings some deviations from linearity of the $H-1/\lambda'$ plot appear and for Dowex 1 X2 the plot is distinctly curvilinear especially at low $1/\lambda'$ values. It is thus clear that the relative contributions to the

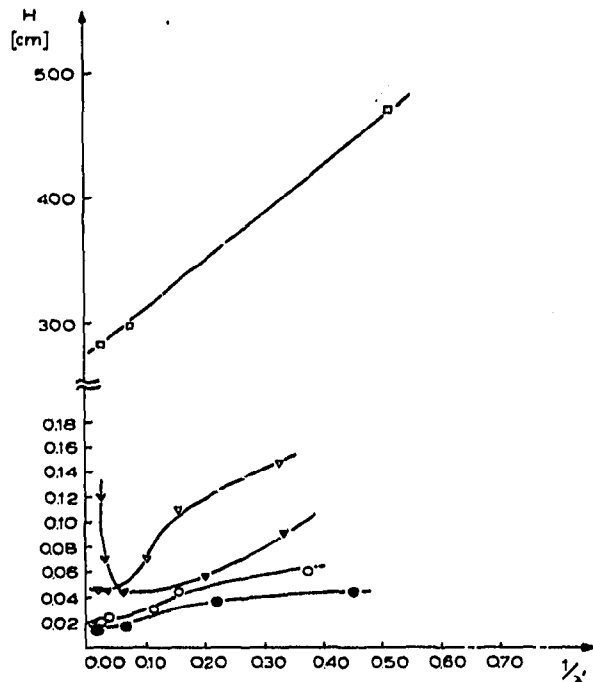
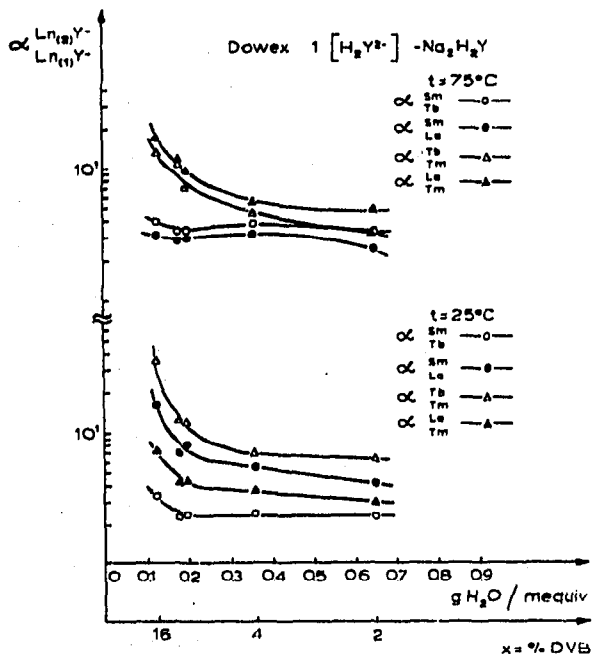


Fig. 7. Separation factors of some rare earths (present as LnY^- anions) on Dowex 1 as a function of the specific water content of the resin.

Fig. 8. Plate height as a function of the reciprocal of bed distribution coefficient for resins of various degrees of cross-linking. ∇ — ∇ —, Dowex 1 X2 [H_2Y^{2-}], temp. 25°; \blacktriangledown — \blacktriangledown —, Dowex 1 X2 [H_2Y^{2-}], temp. 75°; \circ — \circ —, Dowex 1 X4 [H_2Y^{2-}], temp. 25°; \bullet — \bullet —, Dowex 1 X4 [H_2Y^{2-}], temp. 75°; \square — \square —, Dowex 1 X16 [H_2Y^{2-}], temp. 25°.

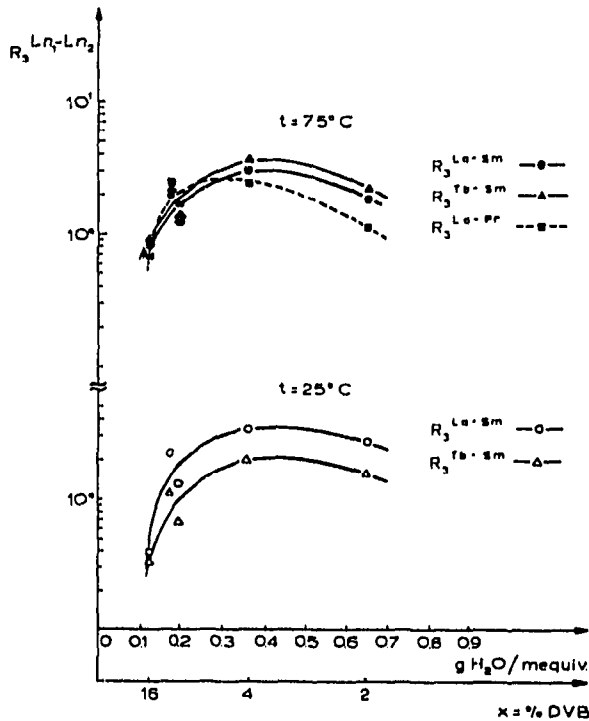
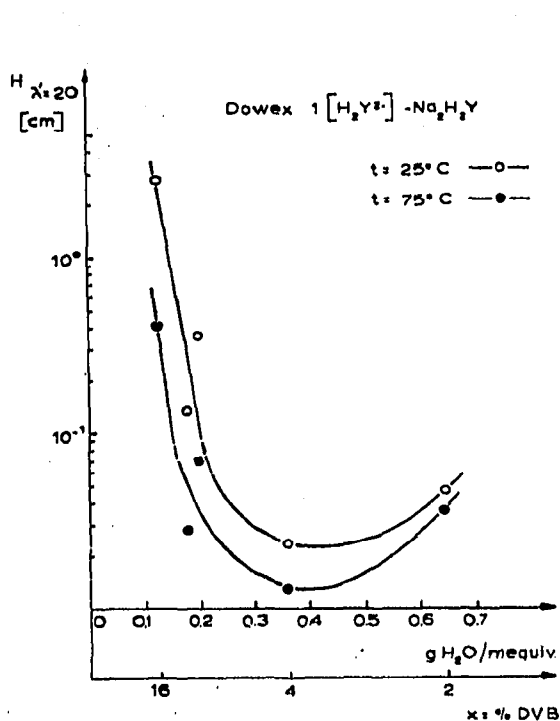


Fig. 9. Plate height, normalized for a bed distribution coefficient value of $\lambda' = 20$, as a function of the specific water content of the resin.

Fig. 10. Resolutions for some rare earth ethylenediaminetetraacetates in the system: Dowex 1 [H_2Y^{2-}]- $\text{Na}_2\text{H}_2\text{Y}$ as a function of the specific water content of the resin.

total plate height of the four terms in eqn. 9, which describe four mechanisms of zone spreading, must change with the variation of cross-linking.

These four terms (from left to right) reflect eddy diffusion, diffusional mass transfer in the resin phase (or "particle diffusion"), diffusional mass transfer in the liquid film (or "film" diffusion), and longitudinal diffusion in the mobile phase, respectively.

Eqn. 9 alone, however, cannot altogether account for such a dependence of the plate height upon resin cross-linking, as was observed experimentally (see Fig. 9). One can easily see that when r_0 , u , and λ' are constant, \bar{D} is the only variable that influences the plate height when a given resin is substituted for another resin of different cross-linking. The variations of the diffusion coefficient in the liquid phase, D , due to the different concentrations of eluant solution employed are usually small, and in the first approximation can be neglected.

As is known from published data^{28,34} diffusion coefficients in the resin phase as a rule decrease with increase in resin cross-linking. The magnitude of this decrease depends on the kind and ionic form of the resin, kind of counterion, its charge, temperature, etc.

At any rate, while one could expect a decrease of plate height with an increase of specific water content (decrease in resin cross-linking) (see Fig. 9), the occurrence of the minimum and the subsequent increase of H with further increase of water content in the resin cannot be explained on the grounds of eqn. 9.

It seems logical, then, to assume that not all the significant mechanisms of zone spreading have been taken into account.

GIDDINGS³⁵ pointed out that under some circumstances longitudinal diffusion in the stationary phase also contributes a significant plate height.

This contribution, denoted here as H_s , is given by the equation³⁵:

$$H_s = \frac{2\gamma_s \cdot \bar{D} \cdot (1-R)}{u \cdot R} \quad (10)$$

where γ_s = obstruction factor which accounts for the fact that diffusion in the stationary phase cannot take place along a direct unobstructed route; and R = ratio of zone velocity to that of mobile phase (= equilibrium fraction of solute in the mobile phase).

Applying the classical MARTIN AND SYNGE equation³⁶ written in terms of the symbols used in ion-exchange chromatography:

$$R = \frac{V}{V + \lambda' \frac{m_j}{d_z}} \quad (11)$$

we obtain:

$$H_s = \frac{2\gamma_s \cdot \bar{D} \cdot \lambda' \cdot m_j}{u \cdot V \cdot d_z} = \frac{2\gamma_s \cdot \bar{D} \cdot \lambda'}{u \cdot i} \quad (12)$$

In this expression the plate height is directly proportional both to the diffusion coefficient in the resin (stationary) phase and to the distribution coefficient.

The separate contributions to zone spreading due to the various mechanisms are additive, so the equation for the plate height in ion-exchange chromatography

can be finally written as:

$$H = 1.64r_0 + \frac{\lambda' \cdot 0.142 \cdot r_0^2 \cdot u}{(\lambda' + i)^2 \cdot D} + \frac{(\lambda')^2 \cdot 0.266 \cdot r_0 \cdot u}{(\lambda' + i)^2 (1 - i) \cdot D (1 + 70r_0 \cdot u)} + \frac{D \cdot i \cdot \sqrt{2}}{u} + \frac{2\gamma_s \cdot \bar{D} \cdot \lambda'}{u \cdot i} \quad (13)$$

Some important experimental facts observed in the present work can be explained on the basis of this equation.

(1) It would be expected that longitudinal diffusion in the resin phase would contribute more to the total plate height, the lower flow rate, the higher distribution coefficient of the eluted species and the lower resin cross-linking (high \bar{D}).

Also, an increase in temperature, which is known to increase the diffusion coefficients^{28,31}, should make the significance of this term more pronounced. If we look at Fig. 8 it is easy to see that these expectations seem to be fulfilled.

While there are no signs of the H_s contribution in the case of Dowex 1 X16, the curves for the lower cross-linked resins become distinctly flattened at low $1/\lambda'$ values, *i.e.* in the region where longitudinal diffusion in the stationary phase becomes most significant. The effect of temperature is particularly characteristic. At high $1/\lambda'$ values where the particle diffusion mechanism still predominates an increase in temperature from 25° to 75° results in a decrease of the plate height for the X2 and X4 resins. As the $1/\lambda'$ diminishes the curves for 25° and 75° come closer together and in the case of Dowex 1 X2 a sharp increase of H at very low $1/\lambda'$ values is even observed. This is a conclusive evidence that some mechanism of zone spreading that is directly proportional to distribution coefficient must be operative.

(2) To evaluate the effect of resin cross-linking on the zone spreading under the conditions when λ' , r_0 , u , i , D , and γ_s , are approximately constant, it is convenient to rewrite eqn. 13 in the form:

$$H = A + \frac{B}{D} + C + E + F \cdot D = (A + C + E) + \frac{B}{D} + F \cdot D \quad (14)$$

where A , B , C , E and F are constants under these circumstances.

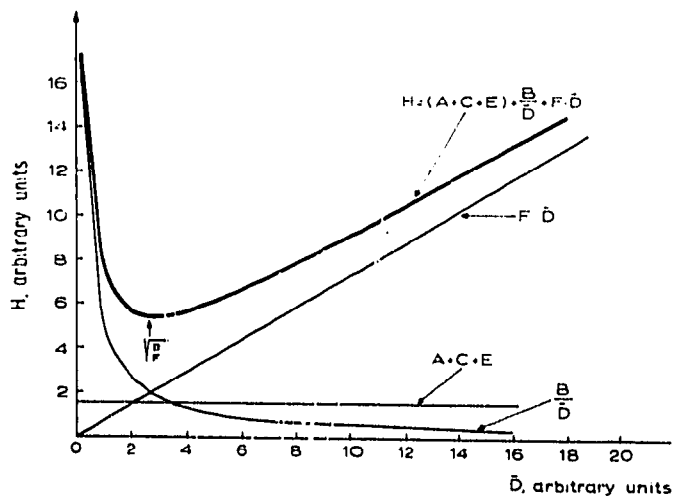


Fig. 11. Schematic representation of the dependence of plate height on the diffusion coefficient in the resin phase.

The schematic representation of the function described by eqn. 14 and its components is given in Fig. 11. As can be seen the curve with a minimum at $\bar{D} = \sqrt{B/F}$ is obtained. Theory thus predicts that with an increase of the diffusion coefficient in the resin phase the plate height at first decreases, passes through a minimum and then increases with the further increase of \bar{D} . To compare this theory with experimental data the functional dependence of the diffusion coefficient on the water content of the resin or some other property which can serve as a measure of cross-linking, would have been needed. Although this is not available it is reasonable to assume that diffusion coefficient increases approximately linearly with the specific water content. The striking similarity of the hypothetical curve on Fig. 11 with the plot of H vs. W_{H_2O}/Z_s (see Fig. 9) shows that this assumption is probably not far from being true. The shape of the curves shown in Fig. 9 confirms the validity of eqn. 13 and is conclusive evidence that the contribution of the longitudinal diffusion in the stationary phase may be significant in ion-exchange chromatography.

The origin of the great changes in plate height with resin cross-linking in the system examined is of interest. In Fig. 12 the corrected selectivity coefficients for the ion-exchange reaction described by eqn. 2 (where: Ln = Tm, La and Sm, respectively) are shown as a function of specific water content. $k'_{H_2Y^{2-}}^{LnY^-}$ at 25° at first regularly increases (Sm, La) or remains constant (Tm), but at higher cross-linkings a sudden drop in the selectivity coefficient values occurs.

This can be interpreted as a result of a sieve effect, *i.e.* partial exclusion of the ions when their dimensions begin to exceed the "pore" dimensions in the resin phase. It is easy to see that the percentage decrease of $k'_{H_2Y^{2-}}^{LnY^-}$ when changing from X8

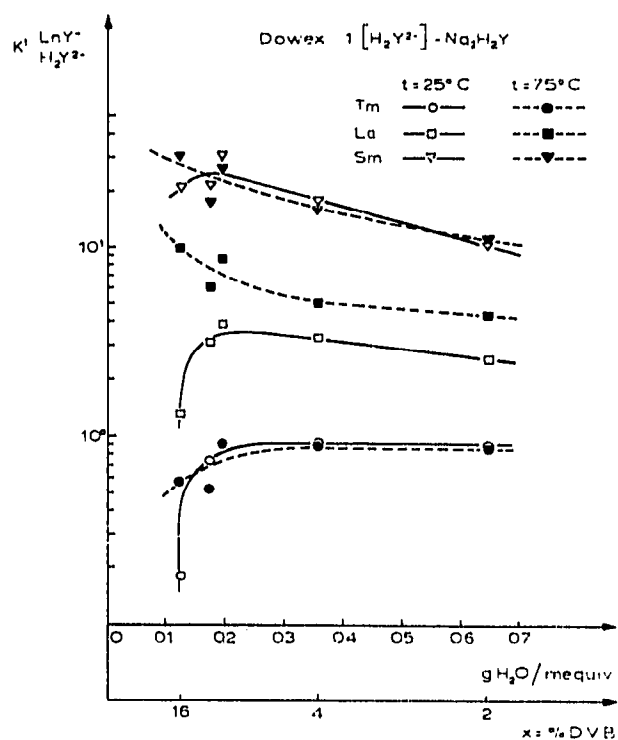


Fig. 12. Corrected selectivity coefficients for the exchange reaction: $1/2 R_2H_2Y + LnY^- \rightleftharpoons RLnY + 1/2 H_2Y^{2-}$ as a function of specific water content of the resin.

to X16 resin increases in the series: Sm < La < Tm (see Fig. 12), *i.e.* in the order of increasing hydrated ionic radii^{13,22,29}.

At 75°, the selectivity coefficients for Dowex 1 X16 increase considerably (see Fig. 12). In the case of Tm, even at this temperature, $k'_{\text{H}_2\text{Y}^{2-}}^{\text{LnY}^-}$ for Dowex 1 X16 is still lower than for medium cross-linked resins, but for La and Sm $k'_{\text{H}_2\text{Y}^{2-}}^{\text{LnY}^-}$ increases over the whole range of cross-linkings (X2-X16) examined.

This is probably caused by the changes in the structure of complex ions with temperature²⁹ and their dehydration, as well as by an increase in elasticity of the polymeric network that increases effective pore dimensions at higher temperatures.

Additional data for the existence of a sieve effect can be derived from Table II. In this table values determined experimentally for exchange capacity in the $[\text{H}_2\text{Y}^{2-}]$ -form are compared with those calculated on the basis of the Z_s values in chloride form (*cf.* Table I). For X2 and X4 resins the differences between the calculated and experimental values are practically within the limits of experimental error, which is of the order of ± 0.04 mequiv./g¹⁵. This difference, however, increases with the rise in resin cross-linking and for Dowex 1 X16 amounts to as much as 0.23 mequiv./g, *i.e.* 14% of the exchange capacity.

TABLE II

EXPERIMENTAL AND CALCULATED^a ION-EXCHANGE CAPACITIES OF ANION EXCHANGERS IN THE ETHYLENEDIAMINETETRAACETATE FORM

Resin	Z_s (mequiv./g dry resin $[\text{H}_2\text{Y}^{2-}]$)	
	Calculated	Determined experimentally
Dowex 1 X2	2.82	2.76
Dowex 1 X4	2.74	2.68
Dowex 1 X8	2.40	2.28
Dowex 1 X10	2.16	2.06
Dowex 1 X16	1.61	1.38

^a Calculated from Z_s values determined experimentally for the resins in question in $[\text{Cl}^-]$ -form (*cf.* Table I).

That means that $\sim 14\%$ of the exchange sites in this resin are completely inaccessible for the H_2Y^{2-} anion. One can expect that LnY^- ions which should be at least as large as H_2Y^{2-} anions will be even more strongly excluded from the resin phase.

An even more pronounced sieve effect was observed in a similar system with rare earth 1,2-diaminocyclohexanetetraacetates³⁷.

The results of the present study clearly show the significance of the proper choice of resin cross-linking in order to realize practical separations.

In the same system a given type of ion-exchange resin may, depending on its cross-linking, yield either excellent separation or virtually no separation at all³⁸ (*cf.* Figs. 3 and 5) although the trend in the values of separation factors is quite the opposite.

This indicates that the common laboratory practice of inferring the possibility

of a separation on the grounds of separation factor values alone, may lead to fallacious conclusions if the interrelation between resin cross-linking and dynamics of chromatographic process is not taken into account.

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