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EFFECT OF RESIN CROSS-LINKING ON THE CATION-EXCHANGE SEPARATION OF ALKALI AND ALKALINE EARTH METALS ON SULPHONIC CATION EXCHANGERS

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SUMMARY

The cation-exchange separation of alkali and alkaline earth metal cations was investigated with resins of 2%, 8% and 16% nominal cross-linking at various temperatures. Selectivity coefficients, separation factors, plate heights and resolutions of adjacent peaks were calculated from column experiments with loads at the trace level. The best separations of alkali metals and of the Ca–Sr pair were achieved at the highest cross-linking (16%), while the medium cross-linked resin (8%) was the best for the separation of the Sr–Ba pair. It was shown that longitudinal diffusion in the stationary phase contributes significantly to the total plate height.

The possibility of predicting the cross-linking at which the minimum value of plate height occurs was demonstrated on the basis of diffusion coefficients, and good agreement with experimental results was obtained.

INTRODUCTION

It has been shown in previous papers that resin cross-linking can have a profound influence on the quality of ion-exchange separation, especially when large complex ions are involved[1–3].

These earlier studies also led to some important generalizations concerning the dynamics of the column process and the mechanism of zone spreading.

It seemed interesting, therefore, to study the effect of resin cross-linking on the cation-exchange separation of simple inorganic ions, such as those of alkali and alkaline earth metals. Only limited data of a rather qualitative character can be found in the literature[4–6]. Preliminary results on the influence of cross-linking on the cation-exchange separation of alkaline earth metals have already been reported[7].

EXPERIMENTAL

Resins

Dowex 50W resins of 2, 4, 8 and 16% nominal cross-linking containing sulphonic acid functional groups were used in this work.

Methods of grinding, fractionating and microscopic determination of particle size have been described earlier[1]. The exchange capacity of strongly acidic groups (Z_s) and the total exchange capacity (Z_c) were determined as described previously[1,8]. The resins were conditioned by successively passing an excess of 1 N HCl and 1 N NaCl solutions through the column filled with the particular resin. After several such cycles, the cation exchanger was completely transformed into the H^+ form by passing a large excess of 1 N HCl solution through it and then washing it with deionized water. The resin was then air-dried and stored in a closed bottle, and its water content was determined by drying it in an oven at 105° to constant weight.

The water contents of swollen resins were determined by the centrifugation method with a specially designed centrifuge tube[2]. A correction for the residual liquid retained at the interface of the beads was taken into account[2].

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

The bed density (d_z) (grams of the dry resin per millilitre of the bed) was determined by introducing a known amount of the resin in deionized water into a graduated cylinder and measuring the volume occupied by the resin bed after settling. The properties of the resin used in this study are summarized in Table I.

Radioactive tracers and reagents

The following radioactive tracers were used: ^{24}Na ($T_{1/2}$ = 15.0 h), ^{42}K ($T_{1/2}$ = 12.4 h), ^{86}Rb ($T_{1/2}$ = 19.5 days), ^{134}Cs ($T_{1/2}$ = 2.3 years), ^{85}Sr ($T_{1/2}$ = 65 days) + ^{89}Sr ($T_{1/2}$ = 51 days), ^{131}Ba ($T_{1/2}$ = 12 days) + ^{133m}Ba ($T_{1/2}$ = 39 h) + ^{135m}Ba ($T_{1/2}$ = 29 h) and ^{45}Ca ($T_{1/2}$ = 153 days).

^{45}Ca with an unknown content of inactive carrier and carrier-free ^{85,89}Sr were obtained from The Centre for Production and Distribution of Isotopes, Swierk, Poland.

The other tracers were prepared by neutron irradiation of the appropriate spectrally pure grade of the chlorides or nitrates in the Polish EWA reactor. When irradiating chlorides, radioactive sulphur and phosphorus were also formed as a result of interfering reactions with fast neutrons: ^{35}Cl(n,p)^{35}S and ^{35}Cl(n,α)^{32}P. These activities were present in anions and as such were found to be useful in determining the free volume of the resin bed and the dead volume of the column.

All the reagents used were of analytical grade.

Apparatus and procedure

Jacketed glass columns of *ca.* 2-mm I.D. were used. A constant temperature (± 0.2°) was maintained by passing water from a Höppler ultrathermostat through the jacket of the column. The eluant solution was supplied to the column from a burette under a mercury column pressure that was regulated so as to obtain the desired flow-rate (0.5–1.0 cm/min).

The effluent was collected in drops on a moving paper band. The drops were then automatically dried when they passed under IR lamps. This apparatus was described in detail earlier[1].

A mixture of tracers was evaporated to dryness in a quartz or glass crucible, dissolved in a small volume (*ca.* 25 μl) of the eluant solution and transferred on to the top of the resin bed. After the "load" soaked into the resin, the mixture was eluted with a hydrochloric acid solution of known molarity at a constant flow-rate.

The dried drops were then counted with an end-window Geiger–Müller counter and elution curves were plotted. The overlapping of the elution curves of particular elements in the K–Rb and Rb–Cs regions was resolved by a second measurement of the ^{86}Rb activity, after ^{42}K had decayed, and γ-spectrometric determination of ^{134}Cs, respectively, as reported earlier[9].

The overlapping Ca and Sr curves were resolved by counting the drops with and without an aluminium absorber (52.6 mg/cm^2). The count rate with the absorber multiplied by a factor of 4.2 gave the true count rate for ^{85,89}Sr. The contribution of ^{45}Ca was found by difference.

In most experiments, the total content of alkali metals in the "load" was very small (less than 0.01% of the total exchange capacity of the resin in a column).

With alkaline earth elements this method was impossible, however, because of difficulties in obtaining the longer-lived barium isotopes of sufficiently high specific activity and because the amount of carrier in the calcium tracer solution was unknown. It was noted during the experiments that when separating alkaline earth elements, the amount of carrier in the sample had a marked influence on the quality of the separation. The conditions were therefore standardized, *i.e.*, the same volume of the stock ^{45}Ca solution was always taken and the amount of barium tracer put on to the column corresponded in each instance to 0.05 mg of Ba. In the experiments with Dowex 50W-X4, another ^{45}Ca tracer solution had to be used because the former one was exhausted. Therefore, only the values of selectivity coefficients were in principle directly comparable with the other results.

The concentrations of the eluant solution for the resins of different degrees of cross-linking were chosen so as to obtain approximately equal bed distribution coefficients for rubidium (alkali metals) and strontium (alkaline earth elements), respectively.

RESULTS

As can be seen from Table I, in which the results for Amberlite IR-120 used in earlier work[8,9] are also included, all the resins were almost monofunctional. A greater difference between the total exchange capacity and that due to strongly acidic groups was observed only in the case of Dowex 50W-X2. The experimentally determined Z_s values were always a little lower than the theoretical capacities (Z_t) calculated by assuming that each aromatic ring originating from styrene carries one functional group. The differences, however, were much smaller than those noted for anion-exchange resins[2].

Similarly, as with anion-exchange resins[2], the water content (W_{H_2O}) and specific

TABLE I

PROPERTIES OF THE RESINS USED

Resin	*Functional groups*	*Exchange capacity (mequiv./g dry resin [H⁺])*				*Density (H⁺ form)*			*Maximum water content*			*Normality of the resin phase, Z_s/W_{H_2O}*	*Particle size (Φ) of the fraction used for column studies*
		Z_s	Z_c	Z_1^a	Z_2^b	d_s	d_j	d_z	H_2O (%)	W_{H_2O} (g H_2O/g dry resin [H⁺])	W_{H_2O}/Z_s (g H_2O/mequiv.)		
Dowex 50W-X2	$-SO_3H$	5.12	5.63	5.35	5.41	1.40	1.40	0.161	74.74	2.959	0.568	1.76	12 μm ≤ Φ ≤ 22 μm
Dowex 50W-X4	$-SO_3H$	5.11	5.20	5.28	5.40	—	1.16	0.273	62.92	1.697	0.332	3.01	13 μm ≤ Φ ≤ 27 μm
Dowex 50W-X8	$-SO_3H$	5.04	5.14	5.14	5.37	1.39	1.21	0.376	50.32	1.013	0.201	4.97	11 μm ≤ Φ ≤ 23 μm
Dowex 50W-X16	$-SO_3H$	4.60	4.73	4.88	5.31	1.42	1.26	0.448	37.15	0.591	0.129	7.78	11 μm ≤ Φ ≤ 21 μm
Amberlite IR-120	$-SO_3H$	5.11	5.15	—	—	1.42	1.24	0.350	50.45	1.020	0.199	5.01	

[a] Calculated by assuming that each aromatic ring originating from styrene carries one functional group.
[b] Calculated by assuming that each aromatic ring originating either from styrene or divinylbenzene carries one functional group.

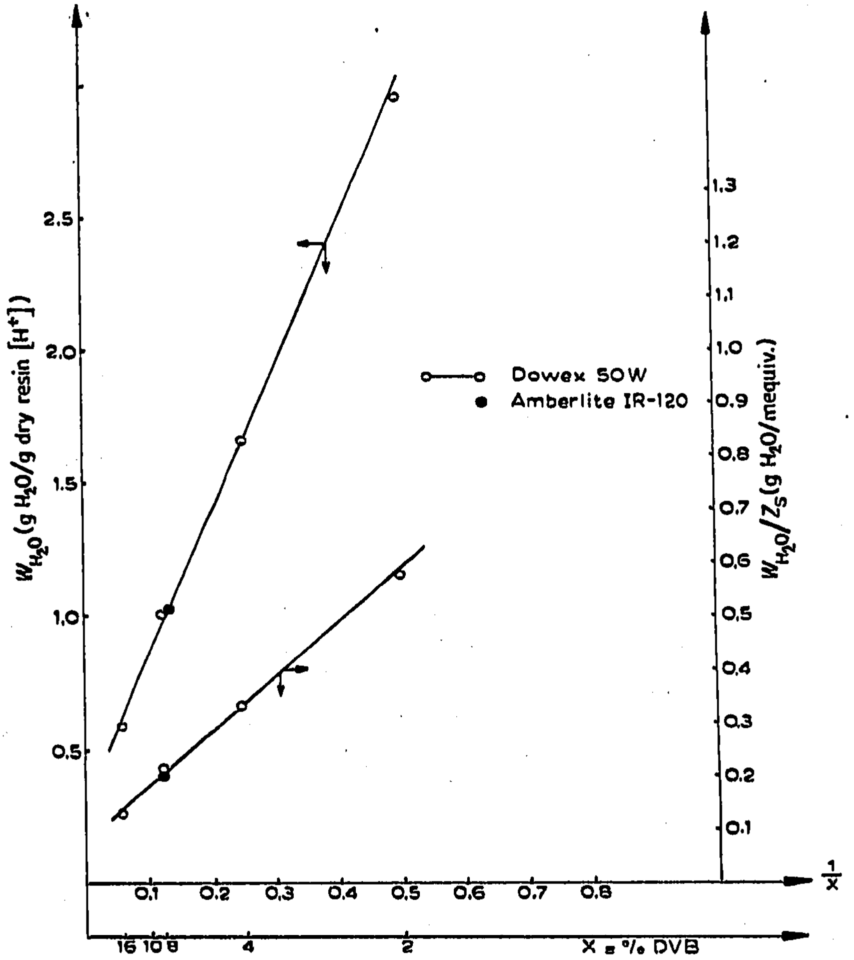

Fig. 1. Water content (W_{H_2O}) and specific water content (W_{H_2O}/Z_S) of Dowex 50W resins as a function of the reciprocal of the nominal divinylbenzene content.

water content (W_{H_2O}/Z_S) were linear functions of the reciprocal of the nominal divinylbenzene content (Fig. 1).

The specific water content was therefore used as a measure of the extent of resin cross-linking. Typical examples of the elution curves obtained at a given temperature with resins of various degrees of cross-linking are presented in Figs. 2–4.

The weight distribution coefficients of metal ions (amount per gram of dry resin (H$^+$ form)/amount per millilitre of solution) were calculated from the elution curves by the equation:

$$\lambda_{Me} = \frac{U_{max.(Me)} - (U_0 + V)}{m_j} = \frac{U_{max.(Me)} - U_{max.(P)}}{m_j} \qquad (1)$$

where $U_{max.(Me)}$ and $U_{max.(P)}$ are the retention volumes (ml) of the metal ion and phosphorus, respectively, U_0 is the dead volume of the column, V is the free volume of the resin bed and m_j is the weight (g) of dry ion-exchange resin in the column.

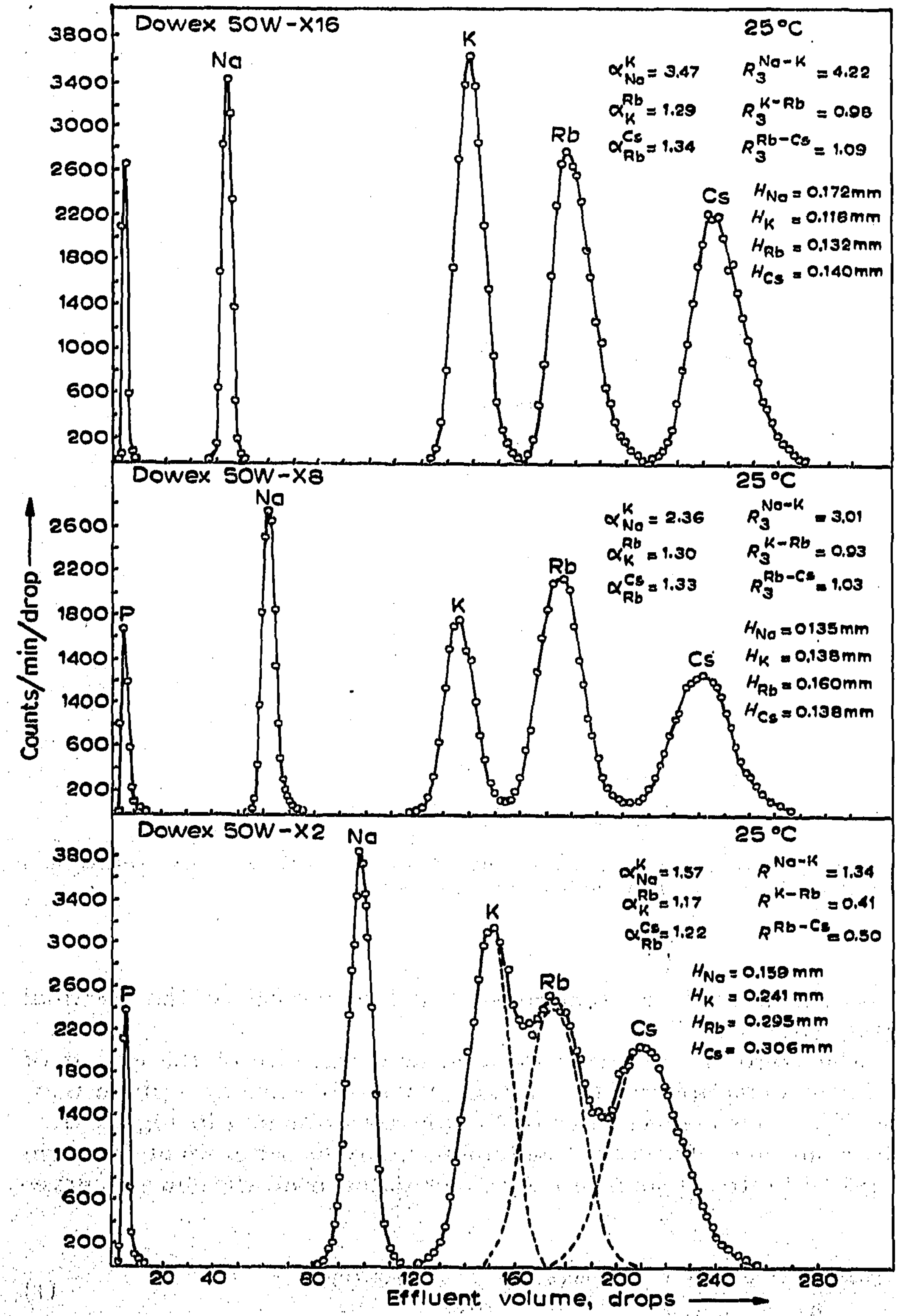

Fig. 2. Effect of resin cross-linking on the separation of alkali metals at 25°. (a) Dowex 50W-X2 [H+] (12 μm ≤ Φ ≤ 22 μm); column, 7.0 cm × 0.0305 cm²; eluant, 0.0679 *N* HCl; flow-rate, 0.72 cm/min. (b) Dowex 50W-X8 [H+] (11 μm ≤ Φ ≤ 23 μm); column, 7.0 cm × 0.0305 cm²; eluant, 0.261 *N* HCl; flow-rate, 0.72 cm/min. (c) Dowex 50W-X16 [H+] (11 μm ≤ Φ ≤ 21 μm); column, 7.0 cm × 0.0305 cm²; eluant, 0.636 *N* HCl; flow-rate, 0.71 cm/min.

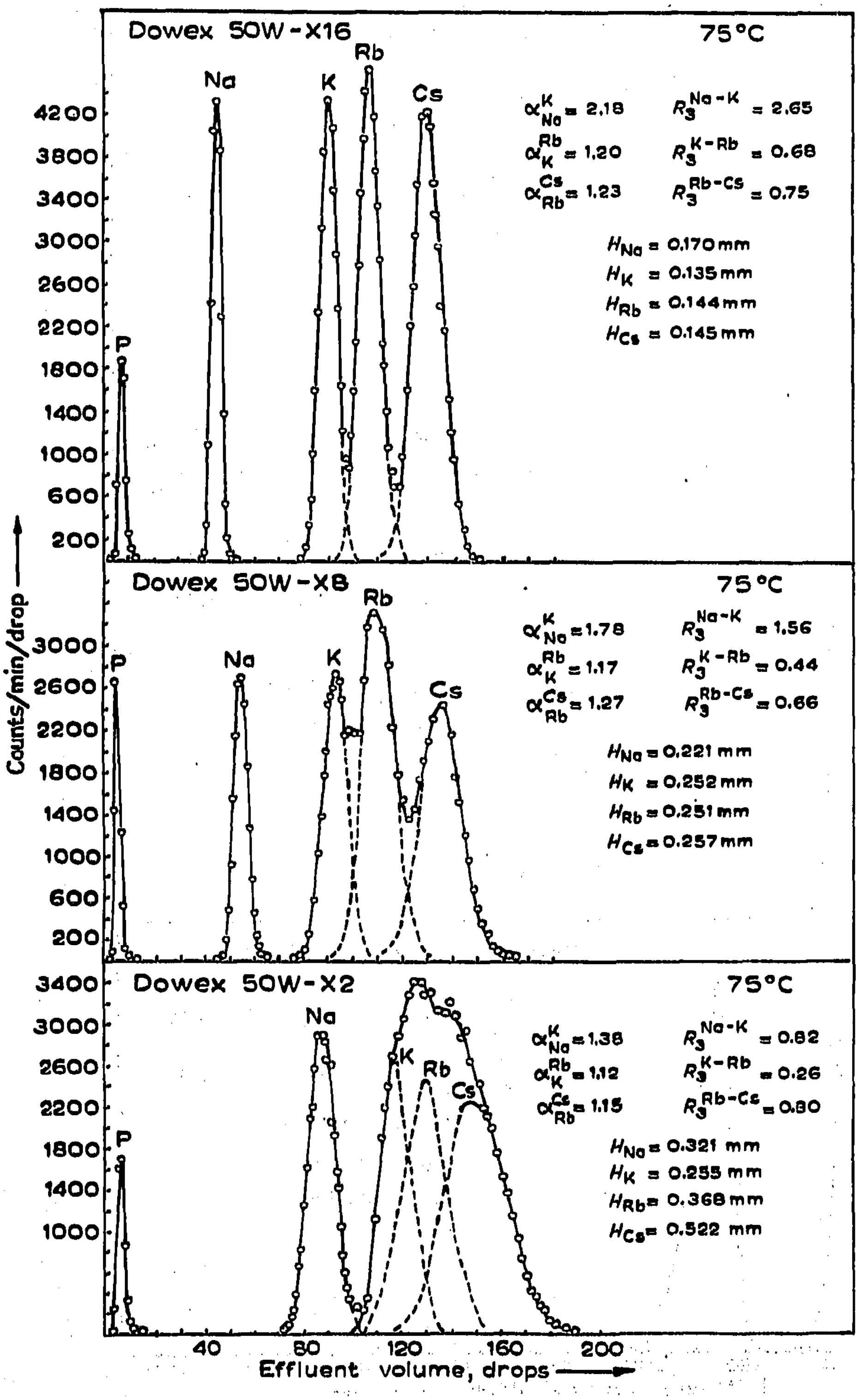

Fig. 3. Effect of resin cross-linking on the separation of alkali metals at 75°. Flow-rate: (a) 0.67 cm/min; (b) 0.66 cm/min; (c) 0.58 cm/min. Other conditions as in Fig. 1.

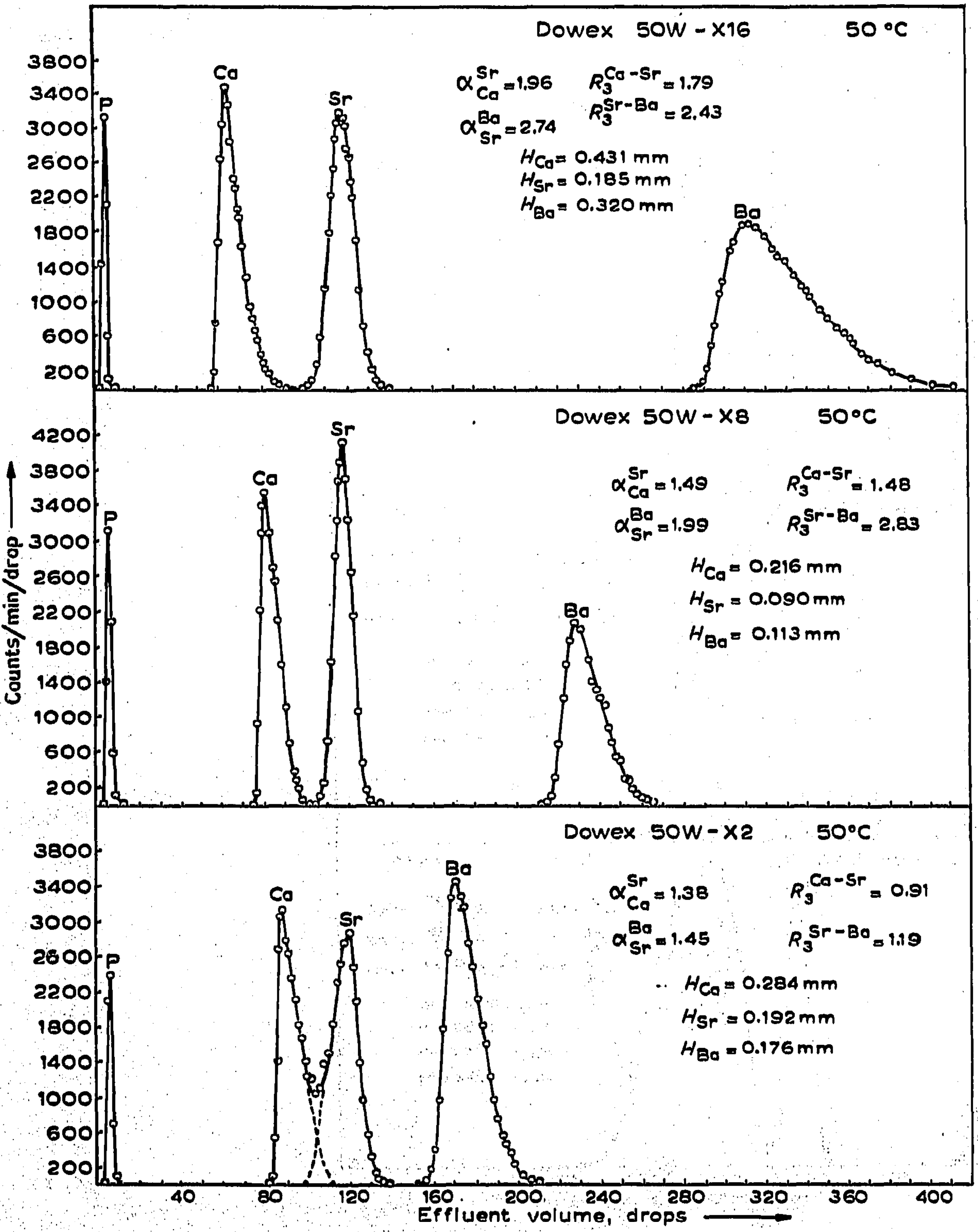

Fig. 4. Effect of resin cross-linking on the separation of alkaline earth elements at 50°. (a) Dowex 50W-X2 $[\mathrm{H}^+]$ ($12\ \mu m \leq \Phi \leq 22\ \mu m$); column, 7.0 cm × 0.0306 cm²; eluant, 0.48 N HCl; flow-rate, 0.71 cm/min. (b) Dowex 50W-X8 $[\mathrm{H}^+]$ ($11\ \mu m \leq \Phi \leq 23\ \mu m$); column, 7.0 cm × 0.0306 cm²; eluant, 1.12 N HCl; flow-rate, 0.74 cm/min. (c) Dowex 50W-X16 $[\mathrm{H}^+]$ ($11\ \mu m \leq \Phi \leq 21\ \mu m$); column, 7.0 cm × 0.0306 cm²; eluant, 2.04 N HCl; flow-rate, 0.74 cm/min.

From these data, selectivity coefficients for the ion-exchange reactions

$$RH + Me^+ \rightleftharpoons RMe + H^+ \tag{2}$$

and

$$RH + \tfrac{1}{2}Me^{2+} \rightleftharpoons \tfrac{1}{2}R_2Me + H^+ \tag{3}$$

were calculated by the equations[1]

$$k_{H^+}^{Me^+} = \frac{\lambda_{Me^+} \cdot C_{H^+}}{Z_s} \tag{4}$$

and

$$k_{H^+}^{Me^{2+}} = \frac{\lambda^{1/2}_{Me^{2+}} \cdot m_{H^+} \cdot d^{1/2}}{Z_s^{1/2}} \approx \frac{\lambda^{1/2}_{Me^{2+}} \cdot C_{H^+}}{Z_s^{1/2}} \tag{5}$$

where m and C denote molality and molarity, respectively, d is the density (close to unity for dilute eluant solutions), and Z_s is the concentration of the resin phase (exchange capacity of strongly acidic groups).

"Corrected" selectivity coefficients, $k'^{Me^{2+}}_{H+}$, were calculated from the relationship:

$$k'^{Me^{2+}}_{H^+} = k^{Me^{2+}}_{H^+} \cdot \frac{\gamma^2_{HCl}}{\gamma^{3/2}_{MeCl_2}} \tag{6}$$

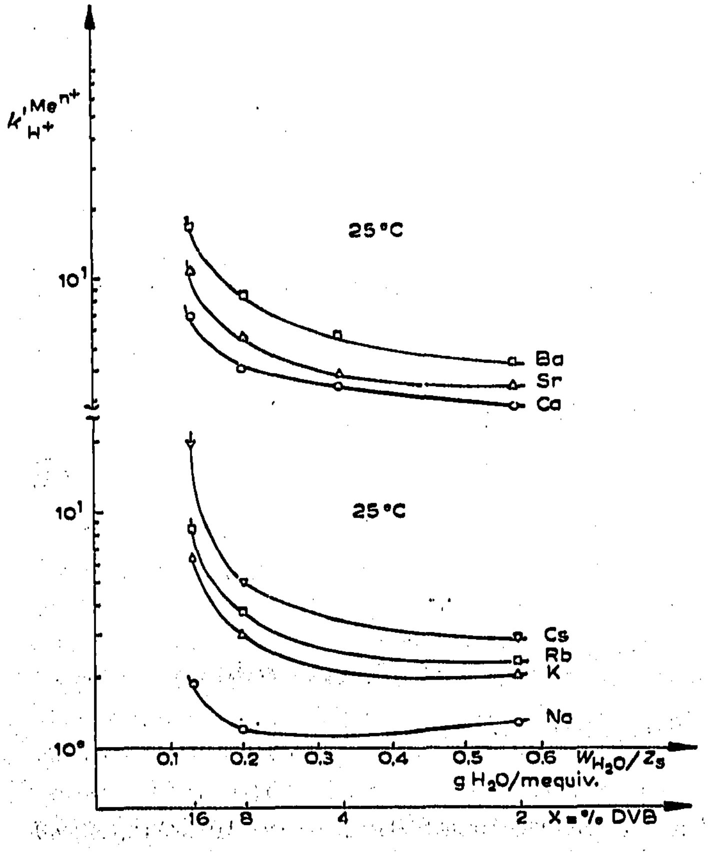

Fig. 5. Corrected selectivity coefficients for the hydrogen ion-exchange reaction for alkali and alkaline earth metal ions as a function of the specific water content of the resin.

where γ denotes the mean activity coefficient that can be derived from the tables published by LIETZKE[10].

Corrected selectivity coefficients of alkali and alkaline earth metal ions are shown in Fig. 5.

Separation factors of adjacent elements are given by

$$\alpha_1^2 = \frac{\lambda_{Me(2)}}{\lambda_{Me(1)}} \tag{7}$$

and are shown in Fig. 6.

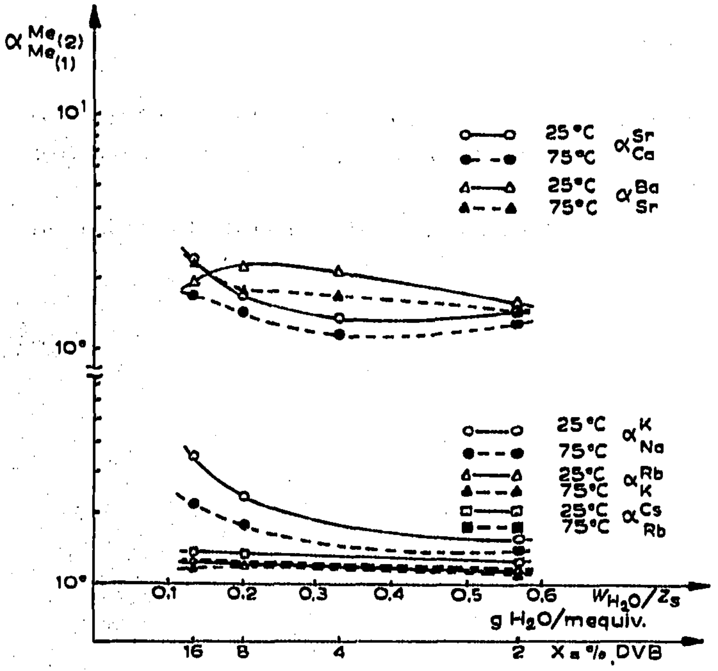

Fig. 6. Separation factors of alkali and alkaline earth metal ions as a function of the specific water content of the resin.

Plate heights were calculated from the relationship[11]

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

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.

Plate heights normalized for the value of the bed distribution coefficient, λ', of 20 ($\lambda' = \lambda \cdot d_z$) are plotted as a function of the specific water content of the resin in Fig. 7.

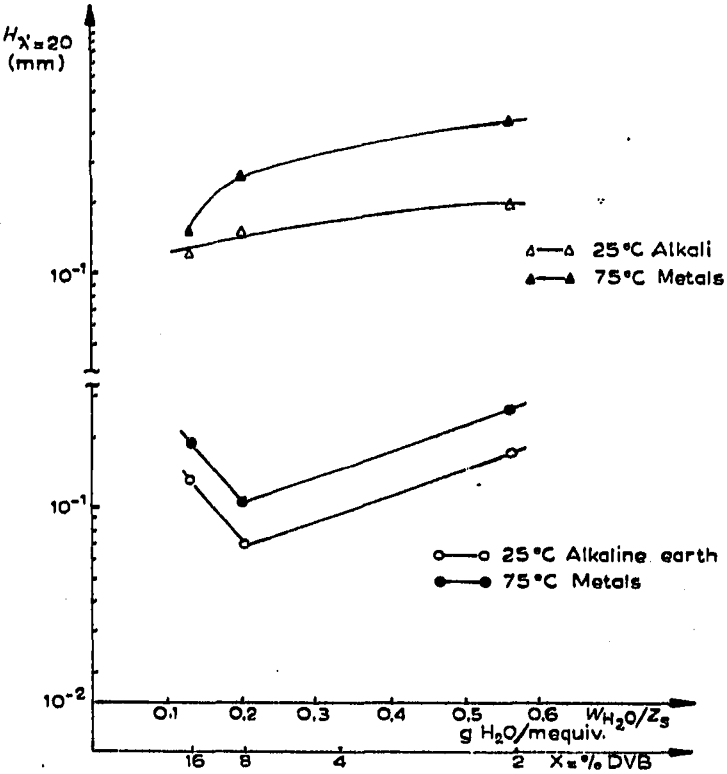

Fig. 7. Plate height, normalized for a bed distribution coefficient value of $\lambda' = 20$, as a function of the specific water content of the resin.

Resolutions of adjacent pairs of elements as calculated from[11]

$$R_s = \frac{U_{\text{max.(2)}} - U_{\text{max.(1)}}}{3(\sigma_1 + \sigma_2)} \tag{9}$$

are shown in Fig. 8.

DISCUSSION

As can be seen in Fig. 5, the selectivity coefficients generally decrease with the increase in the specific water content of the resin, *i.e.*, they increase with the increase in the resin cross-linking.

Only with sodium was a slight minimum at medium cross-linking observed. Separation factors for adjacent alkali metals increase or remain constant with the increase in cross-linking. For alkaline earth elements, the situation is more complex. A distinct maximum occurs on the $\alpha^{\text{Ba}}_{\text{Sr}}$ *versus* W_{H_2O}/Z_s plot at 25°, which disappears at higher temperatures. $\alpha^{\text{Sr}}_{\text{Ca}}$, on the other hand, generally increases with the increase in the resin cross-linking. The minimum visible in Fig. 6 is not definite, as the experiments with Dowex 50W-X4 were performed at different loadings than those for other resins. It is interesting to note that the greatest effect of cross-linking on the separation factor was observed with elements for which the difference in hydration is most pronounced, *e.g.*, the Na–K pair. For divalent ions, not only do hydration–dehydration phenomena and specific interactions between ions and functional groups occur,

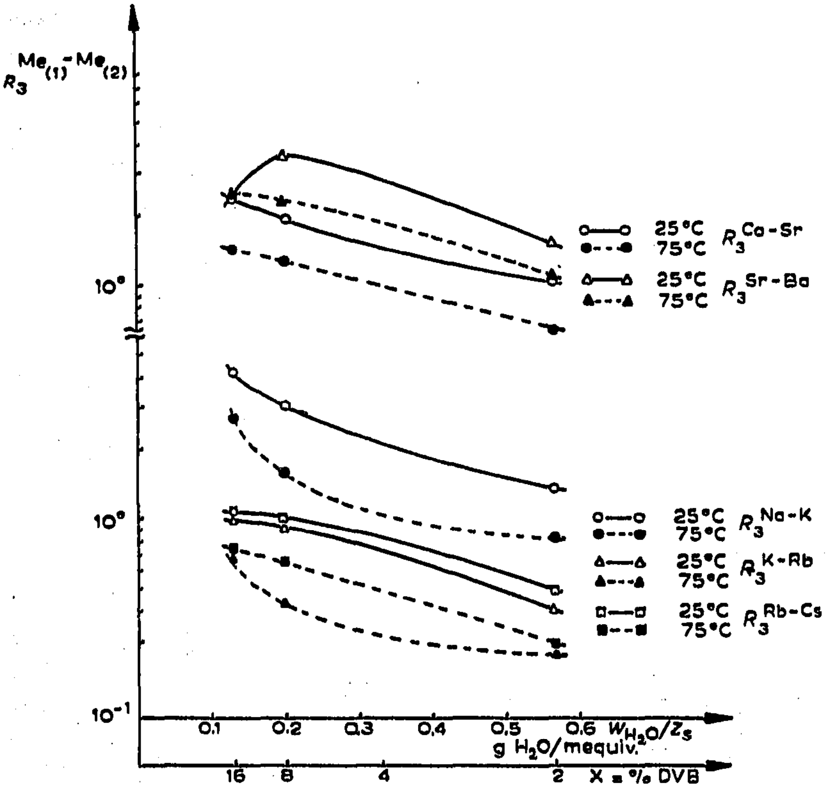

Fig. 8. Resolution for alkali and alkaline earth elements as a function of the specific water content of the resin.

but steric requirements are also probably operative, as the alkaline earth cation must be simultaneously attached to two sulphonic acid groups. At 25°, the resin of medium cross-linking evidently offers the best spatial requirements to discriminate between strontium and barium, and hence the maximum value of separation factor is achieved.

The plate heights, which decrease uniformly with the increase in the resin cross-linking when separating alkali metals, show distinct minima for alkaline earth elements (*cf.* Fig. 7). As has been pointed out earlier[2,3], such a shape of the *H versus* W_{H_2O}/Z_s plot can be explained only if an additional term accounting for longitudinal diffusion in the resin phase is added to the classical Glueckauf equation. The theoretical expression for the plate height can then be written as

$$H = 1.64\,r + \frac{\lambda'\cdot 0.142\cdot r^2\cdot u}{(\lambda'+i)^2\cdot \bar{D}} + \frac{(\lambda')^2\cdot 0.266\cdot r\cdot u}{(\lambda'+i)^2\,(1-i)\cdot D(1+70r\cdot u)} + \frac{D\cdot i\sqrt{2}}{u} + \frac{2\gamma_s\cdot \bar{D}\cdot \lambda'}{u\cdot i} \qquad (10)$$

where

r = mean radius of resin particles
$\bar{D}$ and D = diffusion coefficient in the resin and in the solution phases, respectively
i = fractional free volume of the resin bed
u = linear flow-rate of eluant solution.

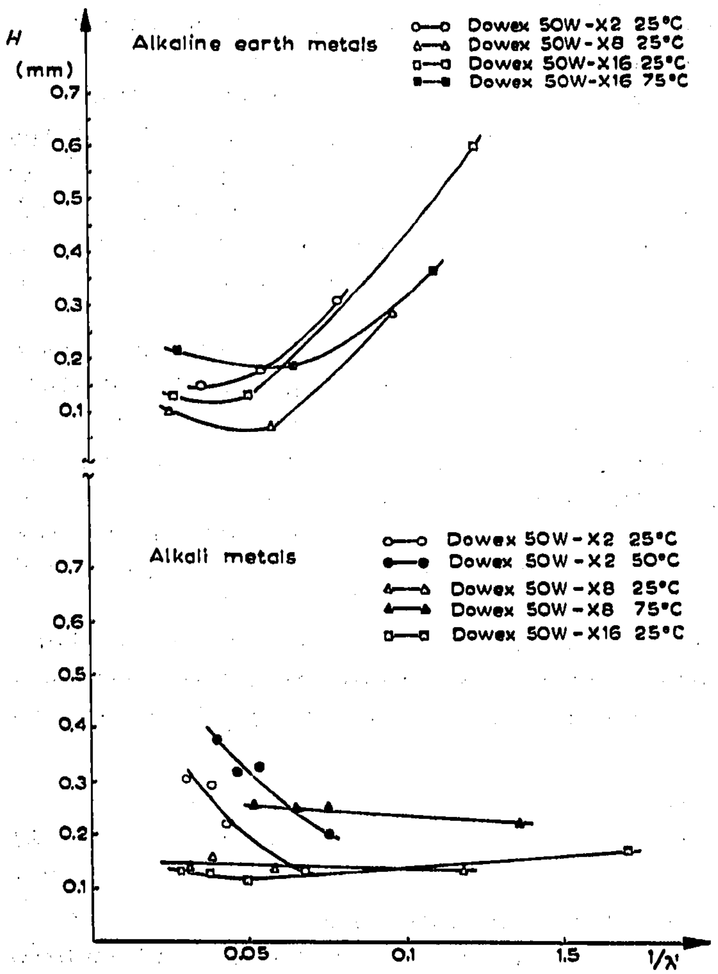

Fig. 9. Plate height as a function of the reciprocal of the bed distribution coefficient for resins with various degrees of cross-linking.

When the diffusional mass transfer in the resin phase (the second term in eqn. 10) is the main factor determining the plate height, as is often the case, then one can expect that H will be a linear function of $1/(\lambda + i') \approx 1/\lambda'$ and will decrease with increase in temperature ($\bar{D}$ is in the denominator).

However, as can be seen from Figs. 7 and 9, in the separation of alkali metals H increases with increase in temperature. This indicates that longitudinal diffusion in the mobile and stationary phases (the fourth and fifth terms in eqn. 10, in which diffusion coefficients are in the numerator), must be operative.

For Dowex 50W-X2 resin, H decreases sharply with the increase in $1/\lambda'$, which again shows the significance of longitudinal diffusion in the resin phase here (the only term in which the distribution coefficient is in the numerator). For Dowex 50W-X8, only a slight decrease of H with the increase in $1/\lambda'$ is observed. A slight contribution of diffusional mass transfer in the resin phase to the plate height occurs with Dowex 50W-X16 resin but only at higher $1/\lambda'$ values (low distribution coefficient values).

These results therefore show good agreement with the theoretical prediction that the contribution of longitudinal diffusion in the resin phase to the total plate height should be the greatest for resins of low cross-linking (high $\bar{D}$), at elevated temperatures and for the higher distribution coefficients of the eluted species.

With alkaline earth elements, the contribution of the mass transfer in the resin phase is much more pronounced because of the considerably lower values of the diffusion coefficients of divalent cations. For example, for Dowex 50W-X4 ($W_{H_2O}/Z_s = 0.359$), values of the diffusion coefficient in the resin phase at 25° of $\bar{D}_{Na} = 1.41 \cdot 10^{-6}$ cm²/sec and $\bar{D}_{Sr} = 2.28 \cdot 10^{-7}$ cm²/sec were reported[12]. However, here also the contribution of longitudinal diffusion can be easily detected (Fig. 9), especially at lower $1/\lambda'$ values.

Comparison of the *H versus* $1/\lambda'$ curves for alkaline earth elements on Dowex 50W-X16 at two temperatures (25 and 75°) clearly shows that at low distribution coefficient values, where mass transfer in the resin phase (the second term in eqn. 10) is predominant, the increase in temperature results in a favourable decrease of plate height. On the other hand, at high distribution coefficient values where longitudinal diffusion in the resin phase (the fifth term in eqn. 10) becomes more important, the plate height increases with increase in temperature, as could have been predicted from eqn. 10.

As has been pointed out in the previous paper[2], if the experiments with resins of various degrees of cross-linking are performed in such a manner that the diffusion coefficient in the resin phase, $\bar{D}$, can be considered to be the only variable, then eqn. 10 can be rewritten in the form

$$H = A + \frac{B}{\bar{D}} + C + E + F \cdot \bar{D} \tag{11}$$

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

Hence one can expect a minimum on the *H versus* $\bar{D}$ curve if resins of sufficiently different extents of cross-linking are included in the investigation.

Diffusion coefficients in the resin decrease rather uniformly with the decrease in the specific water content[12,13]. A similar minimum on the *H versus* W_{H_2O}/Z_s curve is therefore to be expected. As can be seen from Fig. 7, this does occur for the elution of alkaline earth cations. For the elution of alkali metals no minimum was observed, but this would probably occur at even higher extents of cross-linking.

It follows from eqn. 11 that a minimum on an *H versus* $\bar{D}$ plot should occur at $\bar{D}_{\text{min.}} = \sqrt{B/F}$. Comparison of eqns. 10 and 11 leads to the relation

$$\bar{D}_{\text{min.}} = \sqrt{\frac{B}{F}} = \frac{r \cdot u}{\lambda' + i} \cdot \sqrt{\frac{0.142 \cdot i}{2\gamma_s}} \tag{12}$$

According to GIDDINGS[14], obstructive factor values are not known exactly but it is probable that they are of the order of 0.4–0.9. Here the value of $\gamma_s = 0.6$ was assumed. Taking the mean values of $r = 1.5 \cdot 10^{-3}$ cm, $\lambda' = 20$, $i = 0.4$ and $u = 0.7$ cm/min $= 1.1 \cdot 10^{-2}$ cm/sec, one obtains $\bar{D}_{\text{min}} = 1.7 \cdot 10^{-7}$ cm²/sec.

According to literature data[12] for the resin with a specific water content of 0.116 g H_2O/mequiv. (slightly higher cross-linking than for Dowex 50W-X16 resin used in this work, see Table I), $\bar{D}_{Na} = 2.4 \cdot 10^{-7}$ cm²/sec, *i.e.*, it is still higher than the value of $\bar{D}_{\text{min.}}$ calculated above. Diffusion coefficients of the alkali metal cations increase in the order $\bar{D}_{Cs} > \bar{D}_K > \bar{D}_{Na}$. Thus, the $\bar{D}_{min.}$ value could not be achieved with the resins used in this study, and the view that the minimum on the *H versus* W_{H_2O}/Z_s curve should occur at still higher cross-linking is further supported.

Of the alkaline earth metals, the diffusion coeffients of strontium recorded in the literature[12] are $2.28 \cdot 10^{-7}$ cm²/sec for the resin with $W_{H_2O}/Z_s = 0.359$ g H_2O/mequiv. and $3.38 \cdot 10^{-8}$ cm²/sec for the resin with $W_{H_2O}/Z_s = 0.143$. These data indicate that for alkaline earth cations the minimum on the *H versus* W_{H_2O}/Z_s curve should occur somewhere in the vicinity of 8% cross-linking, which was in fact observed experimentally (*cf.* Fig. 7).

In general, however, the variations of plate height with cross-linking when separating simple inorganic ions were much smaller than those noted when large complex ions were involved[2,3].

Resolution, which, as is known, is a quantitative measure of the quality of separation, depends both on the separation factor and the plate height[11]:

$$R_n = \frac{(\alpha_1^2 - 1)\sqrt{L}}{n(\alpha_1^2 + 1)\sqrt{\bar{H}}} \tag{13}$$

where

n = an arbitrary number greater than zero
L = length of the resin bed
$\bar{H}$ = mean plate height.

For alkali metals, the resolution increases monotonically with the increase in cross-linking in the range of cross-linking studied and at all temperatures (*cf.* Fig. 8). This is a consequence of the fact that both the plate height and separation factors change in a favourable direction (case VII of the general classification suggested previously[11]).

The best separations of alkali metals can therefore be achieved with strongly cross-linking resins and at low temperatures. The same is true for the separation of the Ca–Sr pair.

The best separation of the Sr–Ba pair can be obtained with a resin of medium cross-linking (Dowex 50W-X8) at low temperatures, as a result of the simultaneous occurrence of a maximum value of the separation factor and a minimum value of the plate height.

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