

INFLUENCE OF TEMPERATURE ON TRACER-LEVEL SEPARATIONS BY ION EXCHANGE CHROMATOGRAPHY

RAJMUND DYBCZYŃSKI

Department of Analytical Chemistry, Institute of Nuclear Research, Warsaw 9 (Poland)

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The effect of temperature on ion exchange separations has not been investigated in detail. This is rather a strange situation as the temperature should be an important factor influencing the efficacy of chromatographic separations on ion exchangers. As is known, the ion exchange reaction is a diffusion controlled process and a change in temperature has a definite influence on the kinetics of exchange¹. On the other hand the relative affinities of the ions to the exchanger may vary with a change in temperature. This is a consequence of the fact that the enthalpies of individual ion exchange reactions can differ considerably, even if the ions in question are very similar chemically²⁻⁵. It is then clear that the overall effect of temperature on the ion exchange separation of two ions is complex and involves changes both in column performance and in relative ion exchange affinity of the species being separated. The problem of how these factors influence the final separation of the components of a mixture is the object of the present study.

RESOLUTION

The separation of two peaks in elution chromatography can be conveniently represented by the so-called "resolution", R_n , defined as:

$$R_n = \frac{U_{\max(2)} - U_{\max(1)}}{n(\sigma_1 + \sigma_2)} = \frac{\Delta U_{\max}}{n(\sigma_1 + \sigma_2)} \quad (1)$$

where:

$U_{\max(1)}$ and $U_{\max(2)}$ = volumes of effluent at the peaks of components 1 and 2, respectively;

σ_1 and σ_2 = standard deviations of the respective peaks;

n = an arbitrary number greater than 0.

R_2 resolution ($n = 2$) has been currently used in gas chromatography for characterization of separation efficacy⁶. The use of R_3 resolution for the same purpose in ion exchange chromatography was recently proposed⁷. The peak elution volume, U_{\max} , is related to the weight distribution coefficient λ (amount per g of dry resin/amount per ml of solution) by the equation⁷:

$$\lambda = \frac{U_{\max} - (U_0 + V)}{m_j} \quad (2)$$

where:

U_0 = dead volume of the column (ml);

V = free volume of the resin bed;

m_j = weight of the dry ion exchanger resin in the column (g).

The separation factor α (ratio of distribution coefficients of the two species) is thus given by:

$$\alpha_1^2 = \frac{\lambda_2}{\lambda_1} = \frac{U_{\max(2)} - (U_0 + V)}{U_{\max(1)} - (U_0 + V)} \quad (3)$$

Combination of eqns. (1), (2) and (3) yields:

$$R_n = \frac{(\alpha_1^2 - 1)\lambda_1 m_j}{n(\sigma_1 + \sigma_2)} \quad (4)$$

It may be shown^{7,8} that the standard deviation of the chromatographic peak, σ , can be represented by the formula:

$$\sigma = S(\lambda' + i) \sqrt{H \cdot L} \quad (5)$$

where:

S = column cross-section;

H = height equivalent of a theoretical plate;

L = length of the resin bed;

λ' = bed distribution coefficient (amount per ml of the bed/amount per ml of solution); $\lambda' = \lambda \cdot d_z$; where d_z is bed density;

i = fractional free volume of the bed.

As was shown by GLUECKAUF⁹, the plate height H , is not constant and depends on the distribution coefficient of the eluted species. For estimation of resolution however, the respective H_1 and H_2 values can be substituted by the mean plate height:

$$\bar{H} = \frac{H_1 + H_2}{2},$$

then:

$$\sigma_1 + \sigma_2 = S \sqrt{H \cdot L} (\lambda_1' + \lambda_2' + i) = S \sqrt{H \cdot L} (\lambda_1' + \lambda_2' + 0.8) \quad (6)$$

as $i \cong 0.4$.^{7,10}

Introducing eqn. (6) into (4) and taking into account the relation:

$$\lambda \cdot m_j = \lambda \cdot S \cdot L \cdot d_z = S \cdot L \cdot \lambda' \quad (7)$$

we have:

$$R_n = \frac{(\alpha_1^2 - 1) \cdot \lambda_1' \cdot \sqrt{L}}{n(\lambda_1' + \lambda_2' + 0.8) \sqrt{H}} = \frac{(\alpha_1^2 - 1) \sqrt{L}}{n(1 + \alpha_1^2 + 0.8/\lambda_1') \sqrt{H}} \quad (8)$$

For $\lambda_1' > 5$ the ratio $0.8/\lambda_1'$ is sufficiently small to be neglected and we have finally:

$$R_n = \frac{(\alpha_1^2 - 1) \sqrt{L}}{n(\alpha_1^2 + 1) \sqrt{H}} = \frac{(\alpha_1^2 - 1) \sqrt{N}}{n(\alpha_1^2 + 1)} \quad (9)$$

where: \bar{N} = mean number of theoretical plates.

The variation of temperature can influence resolution by changing the separation factor or plate height or both.

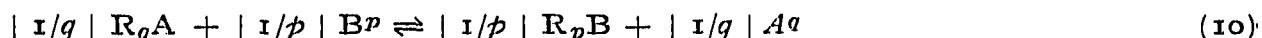
SEPARATION FACTORS

The way in which the α_i^2 value can vary with temperature depends on the ion exchange system employed. KETELLE AND BOYD¹¹ have shown that the separation factors of rare earths as obtained in the course of elution from sulfonic cation exchanger by citrate solutions are virtually independent of temperature. Here, the stability constant values of citrate complexes of particular rare earths are decisive factors for the separation, and their variation with temperature is evidently relatively independent of the lanthanide cation. Moreover, the temperature dependence of cation exchange equilibria for tripositive lanthanides is nearly parallel one with another². It is probable that a similar situation to that with the citrates exists in the case of rare earth elution with other strong complex forming agents.

The separation factors of rare earths in systems such as lactates, α -hydroxyisobutyrate, and especially glycolates show temperature dependence at least for some pairs of elements¹²⁻¹⁴. In these systems complex equilibria in solution as well as in the resin phase are involved and it is difficult to tell which are responsible for the different changes in the distribution coefficients of particular rare earths with temperature.

Very little is known of the effect of temperature on ion exchange separations in the systems where concentrated electrolyte solutions are employed as eluants. A rise in the separation factor of the pair Cr-Mn (α_{Cr}^{Mn}), with the increase in temperature in the system Dowex 2X8[Cl⁻]-concentrated HCl solution, was reported¹⁵. Distinct changes of the separation factors of some lanthanides and actinides, with the increase in temperature in the system Dowex 1[Cl⁻]-concentrated LiCl solution, have been observed¹⁶. The temperature dependence of α_{Am}^{Eu} in the system: Dowex 1 [SCN⁻]-NH₄SCN solution has also been reported¹⁷.

For the systems in which different rates of migration of the components of a mixture down the column are brought about by the differences in their individual ion exchange affinities, the theoretical treatment of the effect of temperature on the separation factor is relatively easy if dilute electrolyte solutions are employed as eluants. For an ion exchange reaction:



where: A^q and B^p are exchangeable ions, q and p their valencies (with appropriate sign for cations and anions respectively), and R is the symbol of the resin matrix.

The selectivity coefficient (equilibrium quotient) is given by:

$$k_{\frac{B^p}{A^q}} = \frac{N_{R_p B}^{|1/p|} \cdot m_{A^q}^{|1/q|}}{N_{R_q A}^{|1/q|} \cdot m_{B^p}^{|1/p|}} \quad (11)$$

where:

N = mole fraction of the ion in the resin phase

m = molality in the solution.

When B^p is present in trace amounts the following relation exists between the distribution coefficient λ_{B^p} and the selectivity coefficient^{4,18}:

$$k_{A^q}^{B^p} = \frac{\lambda_{B^p}^{I/p} \cdot m_{A^q}^{I/q} \cdot d^{I/p}}{C_r^{I/p}} \quad (12)$$

where:

C_r = concentration of the resin phase (mmole per g of dry resin)

d = density of the solution.

$k_{A^q}^{B^p}$ is constant as long as B^p is present in trace amounts and m_{A^q} *i.e.* supporting electrolyte concentration is sufficiently small so that electrolyte invasion of the resin can be neglected.

The separation factor of two ions B^p and D^z is thus given by:

$$\alpha_{D^z}^{B^p} = \frac{\lambda_{B^p}}{\lambda_{D^z}} = \frac{(k_{A^q}^{B^p})^{I/p} \cdot m_{A^q}^{I/q}}{(k_{A^q}^{D^z})^{I/z}} \quad (13)$$

When the charge of the ions being separated is the same (*i.e.*, $p = z$), which is usually the most difficult case, eqn. (13) reduces to:

$$\alpha_{D^p}^{B^p} = \frac{k_{A^q}^{B^p}}{k_{A^q}^{D^p}} \quad (14)$$

The change of selectivity coefficient with temperature depends on the value and sign of the enthalpy:

$$\Delta H_{B^p-A^q}^* = -2.303 R \frac{d \log k_{A^q}^{B^p}}{\left(d \frac{1}{T}\right)} \quad (15)$$

where: R = the gas constant.

$\Delta H_{B^p-A^q}^*$ is the enthalpy change for a differential process in which one equivalent of ions B^p is exchanged for one equivalent of ions A^q (see eqn. (10)), the quantities of both phases being so great that there is neither a resultant change in the composition of either phase nor a transfer of water from one phase to another¹⁰. The standard state for the aqueous phase is the usual hypothetical one-molal solution and that for resin phase the ion exchanger having the desired ionic composition at equilibrium. $\Delta H_{B^p-A^q}^*$ is related to the standard enthalpy change $\Delta H_{B^p-A^q}^0$ by the equation:

$$\Delta H_{B^p-A^q}^0 = \int_{X_{B^p} = 0}^{X_{B^p} = 1} \Delta H_{B^p-A^q}^* d X_{B^p} \quad (16)$$

where: X_{B^p} = equivalent fraction of the ion B^p in the resin. When B^p ions are present in trace amounts the corresponding $\Delta H_{B^p-A^q}^*$ value is a differential quantity for $X_{B^p} \cong 0$.

The values of ΔH^* determined at various temperatures have been reported so

far in the literature for the following exchanges: $\text{Be}^{2+}-\text{H}^+$, $\text{Ba}^{2+}-\text{H}^+$, $\text{Co}^{2+}-\text{H}^+$, $\text{Zn}^{2+}-\text{H}^+$, $\text{La}^{3+}-\text{H}^+$, $\text{Eu}^{3+}-\text{H}^+$, Cs^+-Na^+ , Rb^+-Na^+ , K^+-Na^+ , and $\text{Ba}^{2+}-\text{Na}^+$ on sulfonic resin²; Cs^+-H^+ , Rb^+-H^+ , K^+-H^+ , and Na^+-H^+ on sulfonic and phenolsulfonic resins^{2, 5}; $\text{LnY}^--\text{H}_2\text{Y}^{2-}$ on quaternary ammonium anion exchange resin^{4, 7} (where Ln^{3+} is rare earth cation and Y^{4-} EDTA anion); Br^--Cl^- on quaternary ammonium resin²⁰; and Rb^+-H^+ , Cs^+-H^+ , $\text{Ca}^{2+}-\text{H}^+$, $\text{Sr}^{2+}-\text{H}^+$, $\text{Ce}^{3+}-\text{H}^+$, and $\text{Eu}^{3+}-\text{H}^+$ on zirconyl phosphate³. It follows from these data that ΔH^* can differ considerably even for such chemically similar ions as the alkali metals or rare earth ethylenediaminetetraacetates. Moreover, ΔH^* is usually temperature dependent and can be expressed as:

$$\Delta H^* = \Delta H_0^* + \Delta C_p^* T \quad (17)$$

where: ΔC_p^* = heat capacity change.

Both positive as well as negative ΔC_p^* values have been observed.

In view of the different ΔH^* and ΔC_p^* values for particular ion exchange reactions, the selectivity coefficients also vary in different ways with temperature, and hence according to eqn. (13) the respective separation factors change as well.

It follows from the literature data cited above that the selectivity of the exchanger towards certain ions cannot only diminish, but also increase with the rise in temperature. This indicates that the rule formulated by GRIESSBACH²¹, according to which the selectivity coefficient should always diminish with the rise in temperature, is no longer acceptable.

PLATE HEIGHT

The theoretical expression for the plate height has been derived by GLUECKAUF⁹ and in its most general form is given by^{1, 8}:

$$H = 1.64 r_0 + \frac{\lambda' \cdot 0.142 r_0^2 u}{(\lambda' + i)^2 D_S} + \frac{(\lambda')^2 0.266 r_0 u}{(\lambda' + i)^2 (1 - i) D_L (1 + 70 r_0 u)} + \frac{D_L i \sqrt{2}}{u} \quad (18)$$

where, besides the symbols defined above,

r_0 = radius of ion exchange resin particle;

D_S and D_L = diffusion coefficients in the resin and in solution, respectively;

u = linear flow rate of the eluant solution.

Equation (18) is a representation rather than a means of accurate calculation of H . The H values obtained experimentally are, as a rule, larger than those calculated from eqn. (18) owing to such factors as irregular packing, irregular particle shape, and channelling²². Experimental plate height is obtained from the elution curve by the formula^{7, 23, 24}:

$$H = \frac{L}{N} = \frac{Lw^2 (C + 1)}{8 (U_{\max} - U_0)^2 C} \cong \frac{Lw^2}{8 (U_{\max} - U_0)^2} = \frac{L \cdot \sigma^2}{(U_{\max} - U_0)^2} \quad (19)$$

where, besides the symbols defined earlier:

C = distribution ratio *i.e.* the ratio of the concentration of the substance in the ion exchange resin to the concentration in the solution on one theoretical plate;

N = number of theoretical plates;

w = width of the peak for the $M = M_{\max}/e = 0.368 M_{\max}$ ordinate. The last

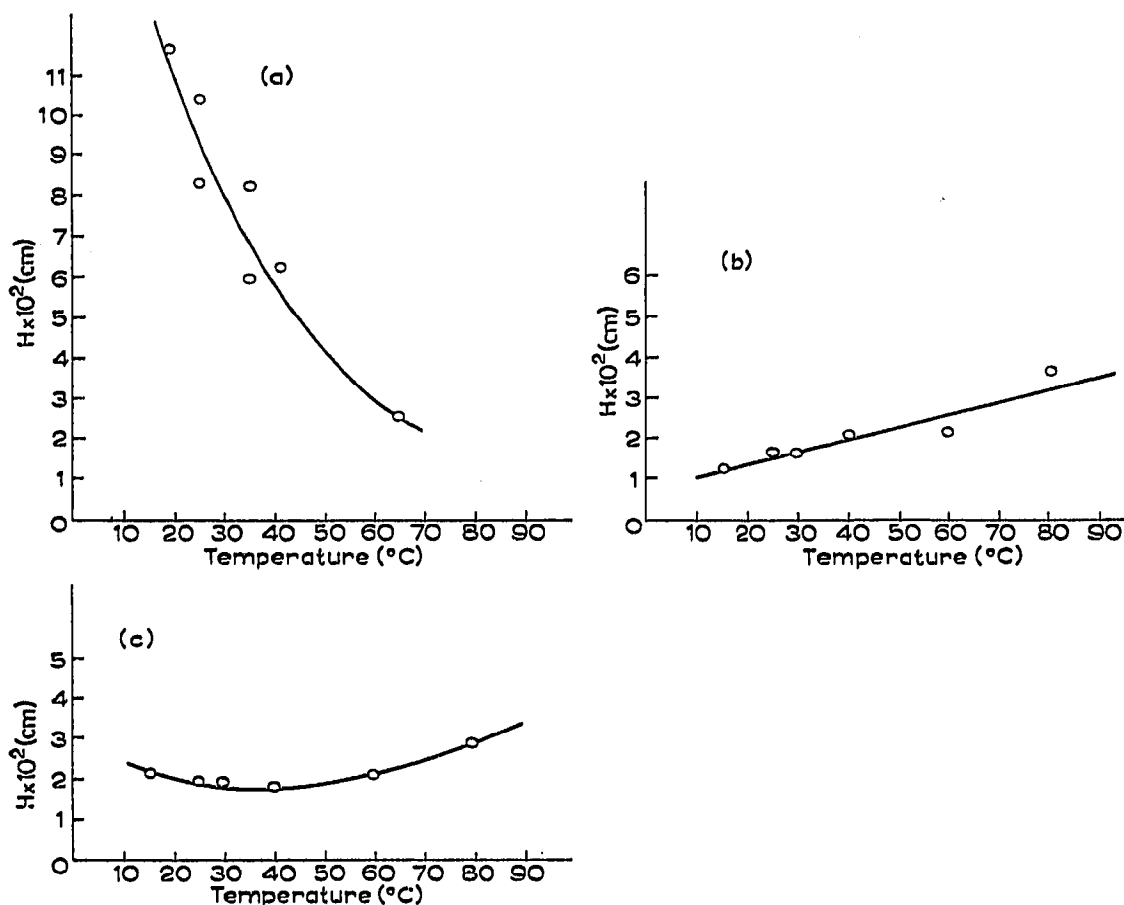


Fig. 1. Plate height normalized for a value of bed distribution coefficient of $\lambda' = 10$, as a function of temperature in various systems. (a) Rare earth ethylenediaminetetraacetates in the system: Amberlite IRA-400[H_2Y^{2-}]- $\text{Na}_2\text{H}_2\text{Yaq}$. Resin particle size: $10 \mu \leq \phi \leq 35 \mu$. Eluant: 0.008–0.009 M $\text{Na}_2\text{H}_2\text{Y}$; $\text{pH} = 4.6$ – 4.7 . Flow rate: $u = 1.08$ – 1.25 cm/min. (b) Alkali metals in the system: Amberlite IR-120[H^+]- HClaq . Resin particle size: $17 \mu \leq \phi \leq 51 \mu$. Eluant: 0.5199 N HCl . Flow rate: $u = 0.47$ – 0.51 cm/min. (c) Alkali metals in the system: cation exchanger MK-3[H^+]- HClaq . Resin particle size: $11 \mu \leq \phi \leq 31 \mu$. Eluant: 0.0712 N HCl . Flow rate: $u = 0.84$ – 0.91 cm/min.

term in eqn. (18) is considered to contribute little to the total plate height, and usually is omitted when presenting this equation^{8,9,22}.

As can be seen, except in the last term, the diffusion coefficients are in the denominator. A rise in temperature increases the diffusion coefficients both in the resin phase and in solution and should bring about a decrease of the plate height. Indeed, better column performance was observed at elevated temperatures when eluting rare earths and actinides from cation exchanger columns with citrates^{11,25}, various hydroxyacids¹³, and EDTA²⁶, as well as with the elution of Fe, Cu, Ni, Co, Mn, Zn, and Cd from a cation exchanger with sulfosalicylate solutions²⁷. A decrease of plate height with a rise in temperature has also been observed when separating rare-earth ethylenediaminetetraacetates by elution with disodium EDTA solutions⁷. The H values calculated from elution curves given in this work⁷ together with some unpublished results are summarized in Fig. 1a.

It has so far been more or less tacitly assumed in the literature^{10,28}, that a rise in

TABLE I

THE POSSIBLE CHANGES IN RESOLUTION, RESULTING FROM SIMULTANEOUS VARIATION OF SEPARATION FACTOR AND OF PLATE HEIGHT

	$\alpha_1^2 \nearrow$	$\alpha_1^2 \leftrightarrow$	$\alpha_1^2 \searrow$
$\bar{H} \nearrow$	(I) $R_n \begin{matrix} \nearrow (a) \\ \leftrightarrow (b) \\ \searrow (c) \end{matrix}$	(II) $R_n \searrow$	(III) $R_n \searrow$
$\bar{H} \leftrightarrow$	(IV) $R_n \nearrow$	(V) $R_n \leftrightarrow$	(VI) $R_n \searrow$
$\bar{H} \searrow$	(VII) $R_n \nearrow$	(VIII) $R_n \nearrow$	(IX) $R_n \begin{matrix} \nearrow (a) \\ \leftrightarrow (b) \\ \searrow (c) \end{matrix}$

temperature should always lead to better column performance. Such a rule although true in many instances is not totally universal. We have found recently, when investigating alkali-metal separation on sulfonic and phenolsulfonic resins²⁰, that in the systems employed the plate height can also increase with an increase in temperature. These data are shown in Figs. 1b and 1c.

It has been suggested²⁰ that the observed increase of H values was due to the longitudinal diffusion contribution (the fourth term in eqn. (18)), which may become important at elevated temperatures especially with resins of a fine mesh size and with relatively slow flow rates.

GENERAL CLASSIFICATION

As has been shown above both separation factor and plate height can either decrease or increase or remain constant with a rise in temperature. Differentiation of eqn. (9) yields:

$$\frac{d R_n}{d \bar{H}} = - \frac{(\alpha_1^2 - 1) \sqrt{L}}{2 \sqrt{\bar{H}^3} n(\alpha_1^2 + 1)} \tag{20}$$

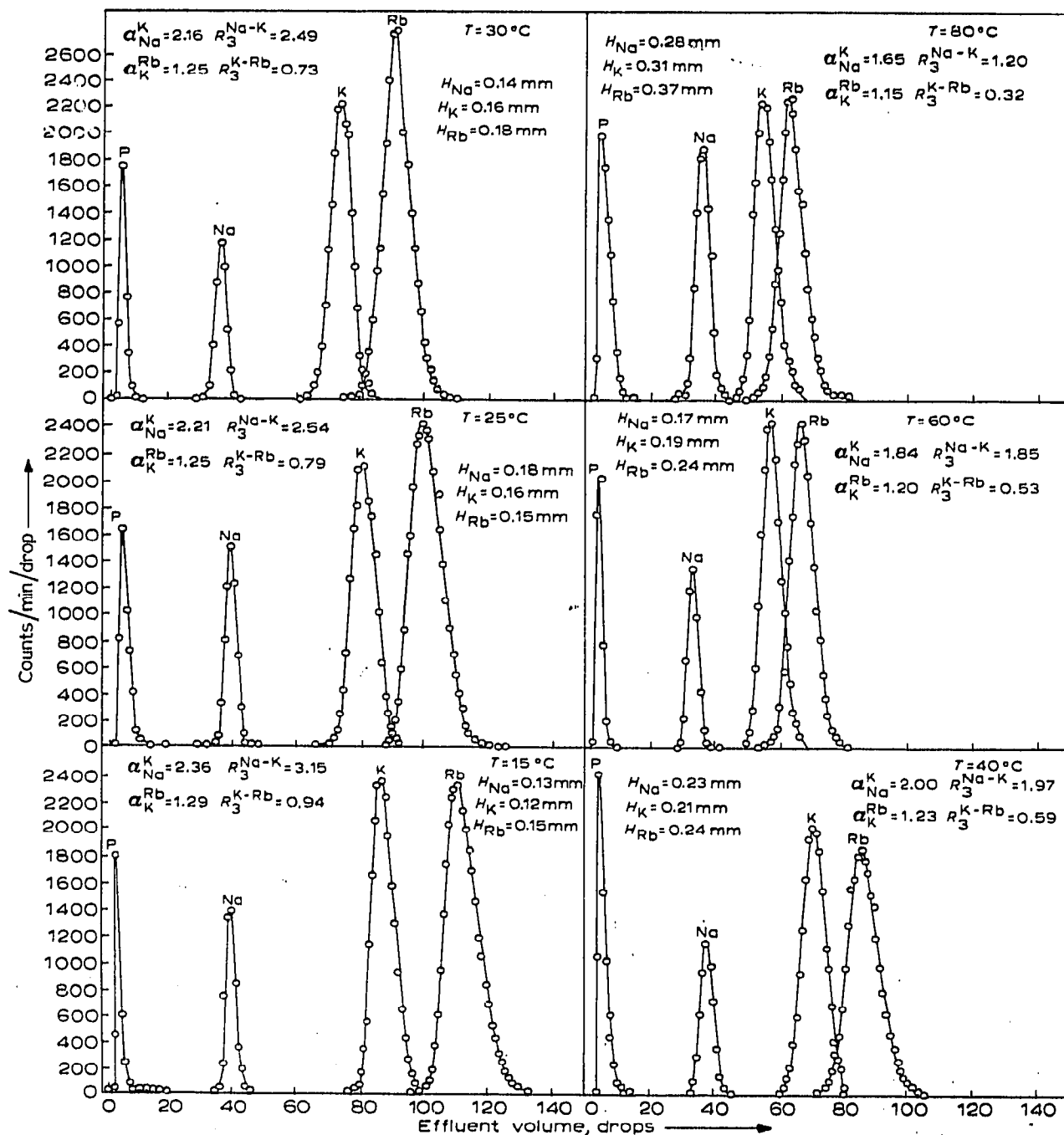


Fig. 2. Influence of temperature on the chromatographic separation of alkali metals. Resin: Amberlite IR-120[H⁺] ($17 \mu \leq \phi \leq 51 \mu$). Column: (a) 7.00 cm \times 0.0330 cm² (runs at 25, 40 and 80°); (b) 6.90 cm \times 0.0330 cm² (runs at 15, 30 and 60°). Eluant: 0.5199 N HCl. Flow rate: 0.47–0.51 cm³/min; from ref. 29.

and:

$$\frac{d R_n}{d \alpha_1^2} = \frac{2 \sqrt{L}}{n \sqrt{H}(\alpha_1^2 + 1)^2} \quad (21)$$

$$\text{For } \alpha_1^2 > 1 \text{ and } \bar{H} > 0, \frac{d R_n}{d \bar{H}} < 0 \text{ and } \frac{d R_n}{d \alpha_1^2} > 0$$

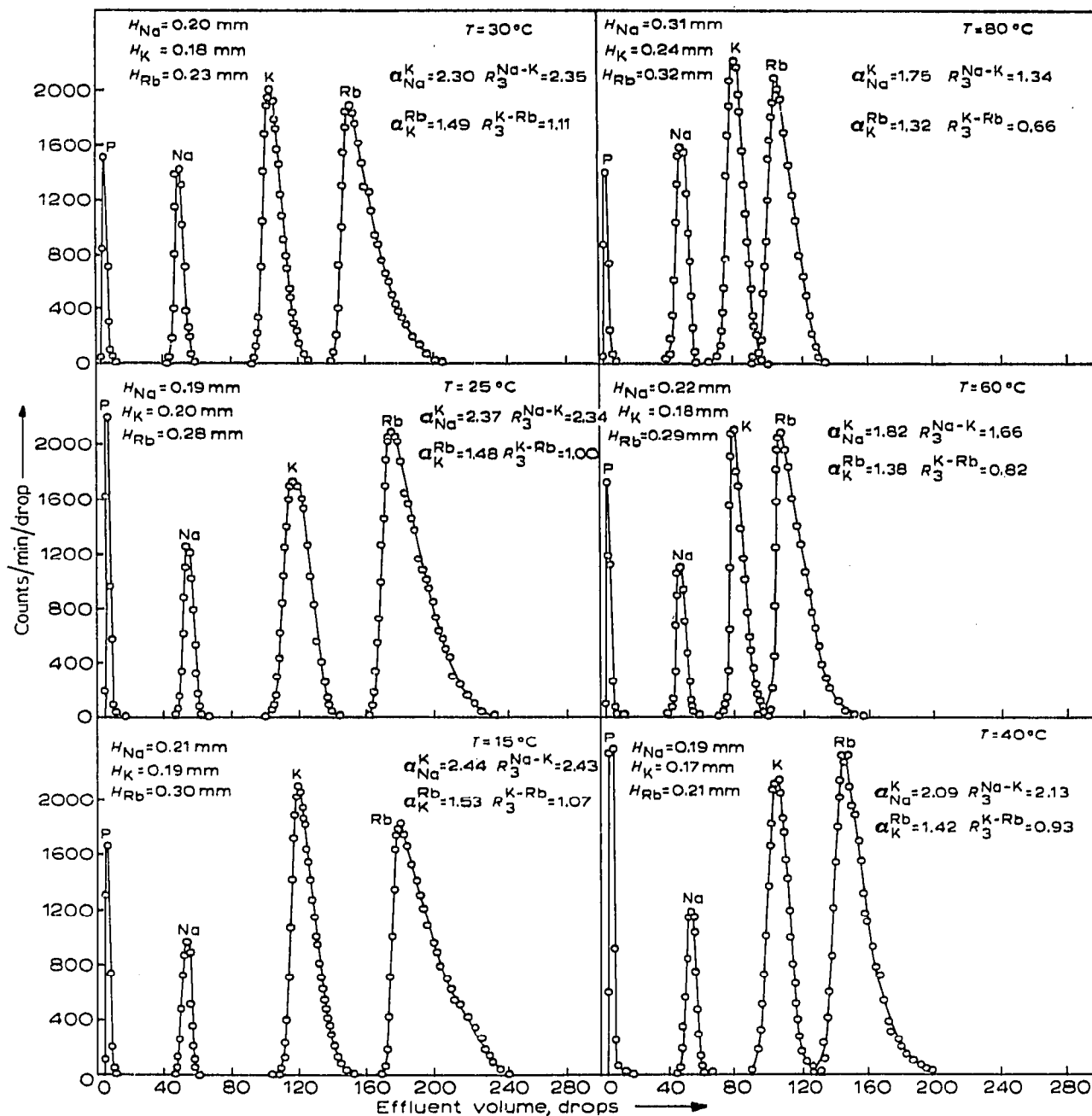


Fig. 3. Influence of temperature on the chromatographic separation of alkali metals. Resin: MK-3[H^+] cation exchanger (phenolsulfonic) ($11 \mu \leq \phi \leq 31 \mu$). Column: 6.00 cm \times 0.0330 cm². Eluant: 0.0712 N HCl. Flow rate: 0.84–0.91 cm/min; from ref. 29.

and hence it follows that with a constant column length, resolution increases with the increase of α_i^j and decreases with the increase of H . The complete set of possible cases is shown in Table I.

As can be seen from Table I, an improvement in resolution is always obtained in cases IV, VII and VIII. In some circumstances, cases I and IX can also lead to better resolution, and this is then when the factor increasing resolution prevails over the other factor acting in the opposite direction. In all other cases resolution diminishes or remains constant.

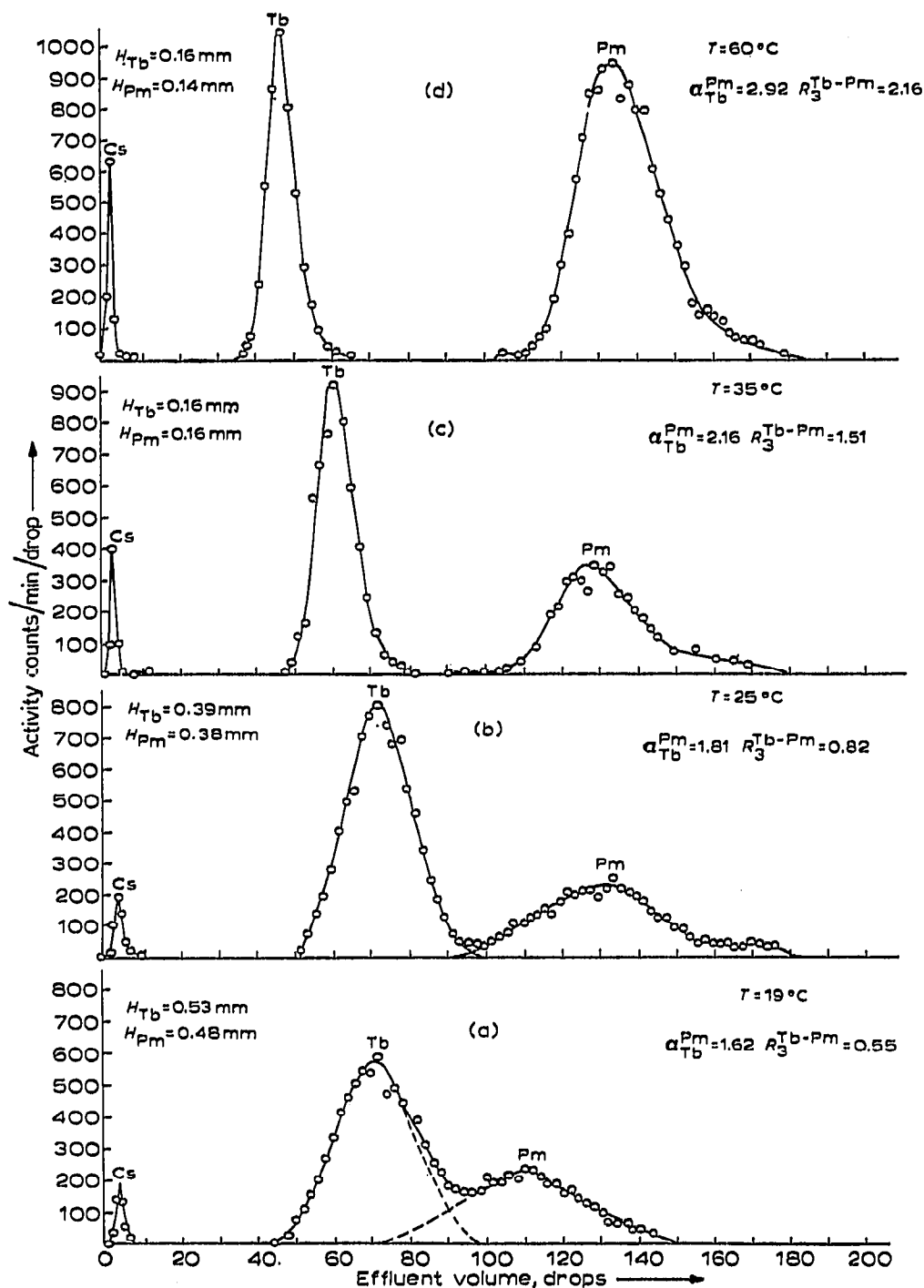


Fig. 4. Influence of temperature on the chromatographic separation of Tb and Pm ethylenediaminetetraacetates. Resin: Amberlite IRA-400[H_2Y^{2-}] ($10 \mu \leq \phi \leq 35 \mu$). Columns: (a) and (b) = 2.50 cm; (c) and (d) = 2.53 cm, cross-section 0.0360 cm^2 . Eluant: for (a) and (b) = 0.0715 M Na_2H_2Y ; for (c) and (d) = 0.0757 M Na_2H_2Y . Flow rate: 1.0–1.2 cm/min; from ref. 7.

EXAMPLES

Several experimental elution curves illustrating the effect of temperature on resolution are presented in Figs. 2–6. H values for the respective peaks were calculated

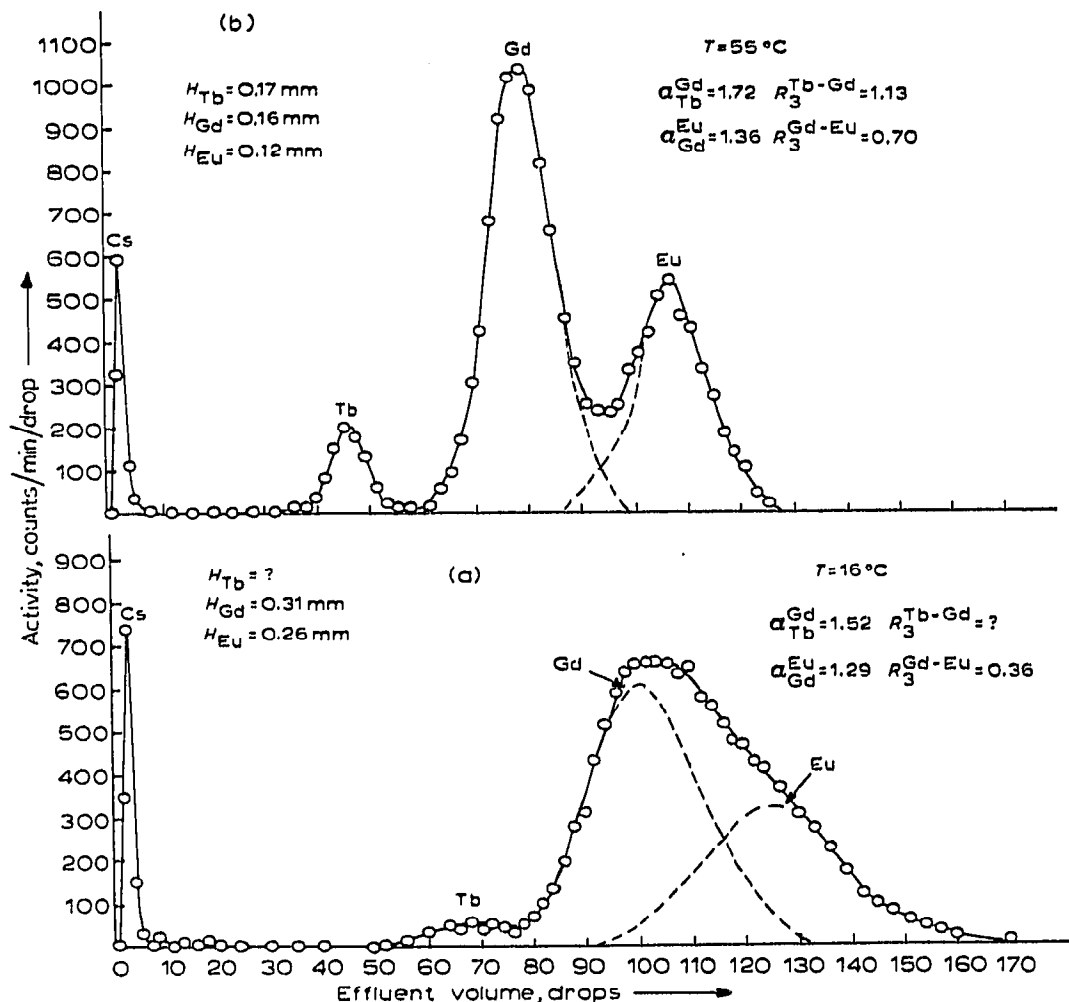


Fig. 5. Influence of temperature on the chromatographic separation of Tb, Gd and Eu ethylenediaminetetraacetates. Resin: Amberlite IRA-400 [H_2Y^{2-}] ($10\ \mu \leq \phi \leq 35\ \mu$). Column: $2.50\text{ cm} \times 0.0360\text{ cm}^2$. Eluant: $0.0769\text{ M Na}_2\text{H}_2\text{Y}$. Flow rate: 1.2 cm/min ; from ref. 7.

from eqn. (19) and the resolutions from eqn. (1). The latter were in most cases in very good agreement with the values of resolution computed from eqn. (9).

The separation of alkali metals on Amberlite IR-120 (Fig. 2) represents generally case III of the classification given in Table I. With a rise in temperature the plate height increases (*cf.* Fig. 1b), the separation factors of the pairs Na-K and K-Rb decrease, and as a result resolution sharply decreases. In the temperature range of $25\text{--}40^\circ$ the separation factor for the pair K-Rb is almost constant; this corresponds to case II. The observed decrease of resolution here is relatively slower as it is due only to the increase of plate height.

Separation of alkali metals on MK-3 resin (Fig. 3) at temperatures $t \geq 40^\circ$ also illustrates case III. In the temperature range of $15\text{--}30^\circ$ however, H slightly decreases (*cf.* Fig. 1c) counterbalancing the effect of a small decrease in $\alpha_{\text{Na}}^{\text{K}}$ and $\alpha_{\text{K}}^{\text{Rb}}$ and the resolution remains nearly constant (case IXb).

Case VII is the most advantageous for the improvement of resolution (simultaneous decrease of H and increase of α_i^2). The separations of Tb-Pm (Fig. 4) and

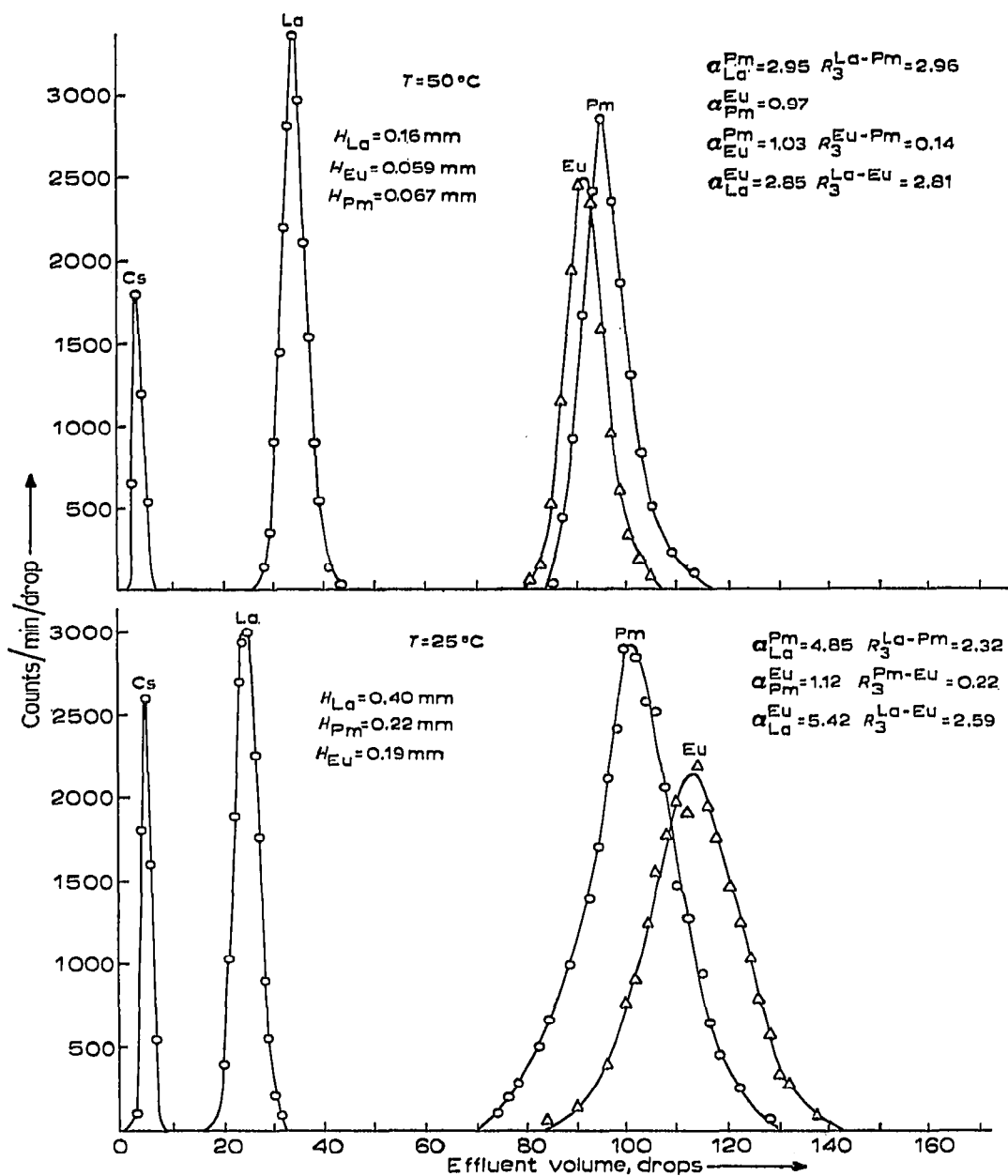


Fig. 6. Influence of temperature on the chromatographic separation of La, Pm and Eu ethylenediaminetetraacetates. Resin: Dowex 1 X₄[H₂Y²⁻] ($11 \mu \leq \phi \leq 42 \mu$). Column: 2.90 cm × 0.0310 cm². Eluant: 0.0393 M Na₂H₂Y. Flow rate: 1.01–1.03 cm/min; from ref. 30.

Tb–Gd (Fig. 5) serve as examples where the resolution sharply increases with the increase in temperature.

The separation of Gd–Eu (Fig. 5) can serve as an example of case VIII. Here the observed increase in α_{Gd}^{Eu} is very small so that as a first approximation the separation factor can be considered as constant. The increase of resolution is thus almost exclusively due to the decrease of plate height with the rise in temperature (*cf.* Fig. 1a). As in this case only one factor acts in a favourable direction, the resolution increases at a slower rate than in case VII.

Sometimes the improvement in column performance with temperature can be so great as to outweigh even the substantial decrease of separation factor. For example, it can be seen from Fig. 6³⁰, that an increase in the resolution of La-Pm, and La-Eu is observed, although a marked decrease of α_{La}^{Pm} and α_{La}^{Eu} occurs (case IX a) at the same time.

The separation of Pm-Eu (Fig. 6) is an interesting example of a case in which a reversal of selectivity occurs. This case as a whole has no analogy in Table I. The classification presented in Table I was derived with the obvious assumption that $\alpha_i^2 > 1$. For $\alpha_i^2 < 1$ the values of resolution are negative, and this does not make sense, because a decrease in resolution would then in fact correspond to a better separation of the two species, the former component 2 being now eluted ahead of former component 1. From the point of view of separation it does not matter which component of a mixture is eluted first, and which second, provided elution curves of both are symmetrical. Therefore the separation of Pm-Eu in the temperature range of 25-50° (see Fig. 6) should be discussed as a composite of two events: in the first temperature subrange α_{Pm}^{Eu} decreases down to a value of $\alpha_{Pm}^{Eu} = 1$, where the corresponding resolution $R^{Pm-Eu} = 0$ (case IXc of Table I); with a further increase in temperature α_{Eu}^{Pm} starts to increase and the resolution R^{Eu-Pm} also increases (case VII). It is worth noting that a very low plate height of approximately $4r_0$ (where r_0 is resin particle radius) was obtained for Eu and Pm peaks in the run at 50° shown in Fig. 6.

PRACTICAL SIGNIFICANCE OF RESOLUTION

The separation of two components of a mixture is taken as being complete if:

$$R_n \geq 1 \text{ i.e. } \Delta U_{\max} \geq n(\sigma_1 + \sigma_2) \quad (22)$$

The choice of n value is arbitrary and depends on the requirements of a given experiment. If the effluent is divided into two fractions at the point: $U = U_{\max} + n\sigma_1$, then the amount of each of the components in its appropriate fraction is given by the area under the normal curve of error:

$$\Phi(n) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^n e^{-n^2/2} dn \quad (n \geq 0) \quad (23)$$

and the impurity amounts to:

$$1 - \Phi(n) = 1 - \frac{1}{\sqrt{2\pi}} \int_{-\infty}^n e^{-n^2/2} dn \quad (24)$$

The values of $\Phi(n)$ for different values of n can be found in the statistical tables³¹. Selected values are shown in Table II.

Using the data from Table II, the result of taking R_3 as a criterion of completeness of separation ($R_3 \geq 1$), means that at least 99.86% of each of the components is in its appropriate fraction and the impurity amounts to at most 0.14% of the peak of the contiguous component. The corresponding figures for $R_2 \geq 1$ are 97.72, and 2.28% respectively etc.

If R_3 is given, the corresponding resolutions for other n values can be calculated from the formula:

$$R_n = R_3 \frac{3}{n} \quad (25)$$

Going back to the examples, it can be calculated from eqn. (25) that separations of Gd-Eu at 55° (Fig. 5), and Tb-Pm at 25° would be considered as complete if R_2 resolution was taken as a criterion of separation.

TABLE II

THE AREA OF NORMAL DISTRIBUTION: $\Phi(n) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^n e^{-n^2/2} dn; (n \geq 0)$

n	$\Phi(n)$	$1 - \Phi(n)$
1	0.8413	0.1587
2	0.97725	0.02275
3	0.998650	0.001350
4	0.99996833	0.00003167
5	0.999999698	0.000000302

On the other hand the separation of the Na-K on Amberlite IR-120 at 60° (Fig. 2) would be still considered as complete even if R_5 resolution was taken as a criterion of separation [$R_5 = R_3(3/5) = 1.85 \times 0.6 = 1.11$] which means that the amount of K in a Na fraction and vice versa is less than $3 \cdot 10^{-5}$ % (cf. Table II).

The conditions for realization of the requirement $R_n = 1$ can be estimated by rearrangement of eqn. (9). When the plate height is known the desired separation factor is given by:

$$\alpha_1^2 = \frac{\sqrt{N} + n}{\sqrt{N} - n} \quad (26)$$

Conversely, the required column length at a given value of α_1^2 is:

$$L = \frac{\bar{H} \cdot n^2 \cdot (\alpha_1^2 + 1)^2}{(\alpha_1^2 - 1)^2} \quad (27)$$

OTHER ASPECTS OF THE CHANGE IN TEMPERATURE

In addition to its influence on resolution, a change in temperature can also affect the time needed for a given separation. At a constant flow rate, the time of elution is proportional to the distribution coefficient of the substance most strongly held by the resin. As has been shown above, the distribution coefficients can depend to a great extent on temperature. It was pointed out in an earlier paper⁷ that sometimes it is worth sacrificing excessively high resolution in order to considerably reduce the time of separation.

In some systems a change of temperature during the elution yields a separation of the "gradient elution" type³².

The rise in temperature has the advantage that it makes operation at higher flow rates possible, which is especially important when using a resin of very fine

particle size. The decrease in pressure which had to be applied to obtain the desired flow rate was shown to be exactly parallel to the analogous decrease of solution viscosity with temperature⁷. On the other hand, operation at elevated temperatures may sometimes lead to undesirable effects such as irreversible changes in the structure of the exchanger²⁰ or formation of air bubbles in the column.

CONCLUSIONS

As has been shown above, the temperature is an important factor influencing the quality and ease of separation by ion exchange chromatography. By controlling the temperature during the operation one can greatly influence the resolution of chromatographic peaks, and in some cases even change the order of elution. Further work is needed to learn more about the temperature dependence of distribution coefficients of elements and substances in various systems, and about factors influencing the plate height.

An important application of ion exchange chromatography performed at different temperatures, namely the qualitative identification of elements and substances on the basis of the $\log k_{Aq}^{Bp} - 1/T$ plot has been reported¹⁸.

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SUMMARY

The effect of temperature on the separation of trace amounts of substances by ion exchange chromatography is discussed. The overall influence of temperature on the final resolution of chromatographic peaks consists of corresponding contributions due to the changes of separation factor and of plate height. Both separation factor and plate height can either decrease or increase or remain constant with a rise in temperature depending on the species to be separated and the ion exchange system employed.

A general classification of possible changes in resolution resulting from the variation of separation factor and plate height has been given, and numerous examples are presented.

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