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## EXPERIMENTAL STUDY OF SELECTIVITY AND COLUMN EFFICIENCY IN CLATHRATE CHROMATOGRAPHY USING WERNER COMPLEXES AS CLATHRATE HOST COMPONENTS

### II. OPTIMIZATION OF OPERATING PARAMETERS

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#### SUMMARY

The column efficiency has been studied in liquid chromatographic systems with  $\beta$ -Ni(NCS)<sub>2</sub>(4-MePy)<sub>4</sub> clathrates as the stationary phase. It was found that peak broadening is determined mainly by the diffusion processes within the clathrate crystals. The relative values of the diffusion coefficients of *o*-, *m*- and *p*-dinitrobenzene isomers as a function of clathrate structure parameters have been estimated using Giddings theory. It was found experimentally that the optimum efficiency can be obtained with small particles of 5–10  $\mu$ m diameter and low flow-rates, less than 10 ml/h. This limitation in flow-rate is acceptable because of the high selectivity of the  $\beta$ -clathrate; thus 3–4 cm long columns are sufficiently efficient.

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#### INTRODUCTION

In a previous paper<sup>1</sup> we reported the selectivity in clathrate liquid chromatography (LC), when using the  $\beta$ -Ni(NCS)<sub>2</sub>(4-MePy)<sub>4</sub>\* clathrate as the solid phase. We have now investigated the characteristic features of the system from the point of view of its efficiency, so as to enable an optimization of the experimental conditions of separation.

The main problem was to determine the mechanism of separation, *i.e.*, the rate determining step in the processes of sorption and desorption which occur during chromatographic separations. So, the questions we wish to answer are:

Do molecules of sorbate adsorb on the surface of the clathrate sorbent only, or do they penetrate the whole volume of the sorbent.

If the molecules of the sorbate do penetrate the volume of the clathrate sorbent, which of the two processes, surface adsorption or diffusion in the solid phase is the slowest.

The physicochemical background to this study has been given in recent papers on crystal structure analysis<sup>2,3</sup>, thermochemistry<sup>4,5</sup> and kinetics<sup>6</sup> of clathration with the Ni(NCS)<sub>2</sub>(4-MePy)<sub>4</sub> complex.

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\* 4-MePy = 4-methylpyridine.

## THEORETICAL

Following the Giddings<sup>7</sup> general non-equilibrium theory of bed efficiency, the overall plate height ( $H$ ) can be expressed as

$$H = A + \frac{B}{U} + C_{k,s} \cdot U + C_m \cdot U \quad (1)$$

where  $A$  represents eddy diffusion flow profile effects,  $B$  the longitudinal diffusion,  $U$  the flow-rate of the mobile phase and  $C$  the mass-transfer contributions defined as:

$$C_{k,s} = q \cdot t_d \cdot \frac{k'}{(1 + k')^2} \quad (2)$$

and

$$C_m = \omega \cdot \frac{d_p^2}{D_m} \quad (3)$$

where  $C_{k,s}$  represents mass transfer controlled by adsorption-desorption kinetics and/or diffusion in the stationary phase,  $C_m$  the mass-transfer contribution in the mobile phase,  $k'$  the capacity factor,  $q$  a geometrical factor,  $t_d$  the time which the solute spends linked to the stationary phase,  $\omega$  a structural parameter,  $d_p$  the particle size and  $D_m$  the diffusion coefficient of the solute in the mobile phase.

Detailed analysis of eqn. 1 and the different contributions to the plate height ( $H$ ) may be found in monographs (e.g., ref. 8). For the purpose of the present study we concentrate on the  $C_{k,s}$  term which is directly related to the questions given in the Introduction. First, we can study the relation between the distribution coefficient ( $K_g$ ) and particle size ( $d_p$ )

$$K_g = \frac{V_R'}{m}$$

where  $V_R'$  is the net retention volume per gram of the sorbent and  $m$  is the mass of the sorbent. An increase of  $K_g$  may be expected if the surface area of the stationary phase increases (surface adsorption); alternatively, if there is no such effect we refer to the term (volume absorption). Having made this distinction and when analyzing the  $C_{k,s}$  term on the basis of experimentally found  $k'$  and  $H$  data and the Giddings theory, we may then try to distinguish between adsorption and absorption mechanisms.

## EXPERIMENTAL

*Preparation of the sorbents*

The clathrate sorbents of appropriate particle size were prepared by their precipitation from aqueous organic solvent solutions at constant temperature ( $25 \pm 1^\circ$ ). Aqueous solutions of  $\text{Ni}(\text{NCS})_2$  (0.2 M) and 4-MePy were poured into mixtures of organic solvent,  $\text{NH}_4\text{SCN}$  and water with flow-rates varying from 3 to 150 ml/h. Acetone (Ac) or ethanol (Et) was used as the organic solvent. At high precipitation

speed a fine powder of *ca.* 10  $\mu\text{m}$  was obtained, but slow precipitation led to the formation of *ca.* 60  $\mu\text{m}$  crystals. The products were then fractionated by sieving in the mother liquor. Particle sizes were checked microscopically.

In the following text, the concentrations of the organic solvents and of 4-MePy in the mobile phase (mother liquor) are indicated in terms of the abbreviations for the clathrate sorbents, *e.g.*, Et 40/1.5 denotes the  $\text{Ni}(\text{NCS})_2(4\text{-MePy})_4 \cdot \text{G}$  sorbent (G = guest) equilibrated with aqueous ethanol (40%, v/v) containing 4-MePy (1.5%, v/v).

#### Analytical determinations

The results of phase analysis, refinement of lattice parameters and determinations of the guest content in the clathrates used in the present study were reported previously<sup>1</sup>; the same abbreviations have been used.

#### Chromatographic experiments

Glass columns (30, 60 and 90  $\times$  5 mm I.D.) were prepared by slurry packing. The flow-rate of the mobile phase was varied from 2 to 25 ml/h.

Values of the distribution coefficient ( $K_g$ ), capacity factor ( $k'$ ), the plate height ( $H$ ) and the resolution ( $R_s$ ) of two adjacent peaks 1 and 2 were calculated from  $K_g = (V_R - V_0)/m$ ,  $k' = (V_R - V_0)/V_0$ ,  $H = L/N$ ,  $N = (V_R/\sigma)^2$  and  $R_s = (V_{R1} - V_{R2})/2(\sigma_2 + \sigma_1)$ ; where  $V_R$  is the retention volume,  $V_0$  the volume of the mobile phase in the column, calculated as the retention volume of furazol,  $m$  the amount of clathrate sorbent in the column,  $L$  the length of the column,  $N$  the number of theoretical plates and  $\sigma$  the standard deviation of a Gaussian peak.

LC separation of *ortho*, *meta* and *para* isomers of dinitrobenzene was studied as a function of the operating parameters (particle size, flow-rate, column length) and porosity (free volume) of the clathrate host structure.

## RESULTS AND DISCUSSION

In Fig. 1 the plate height ( $H$ ) is plotted against the capacity factor ( $k'$ ). As may be seen, the plate height is a function of  $k'$  and shows a maximum when  $k' = 1$ . This pattern is typical for systems in which mass transfer in the stationary phase is the rate determining step; here the  $C_{k,s}$  term is only dependent on  $k'$  and has a maximum at  $k' = 1$  (see eqn. 2). It has also been found that the distribution coefficient, given as the retention volume per gram of sorbent, is independent of the particle size of the clathrate sorbent (see Fig. 2). In other words it is independent of the surface area of the crystals. This suggests that sorption involves the whole volume of the solid phase, not only its surface. Both these conclusions indicate that the efficiency of the clathrate columns is limited by the stationary phase mass-transfer effects.

According to theory<sup>7</sup>, the contribution of  $C_{k,s}$  to the plate height ( $H$ ) would be linearly dependent on  $d_p$  if the surface adsorption were rate limiting, or on  $d_p^2$  if diffusion in the stationary phase were the slowest step of the process. This statement is, however, of no practical importance when analyzing differences in the relationship between plate height ( $H$ ) and particle size ( $d_p$ ) from the point of view of selecting the adsorption or absorption mechanism. This is because other contributions to the plate

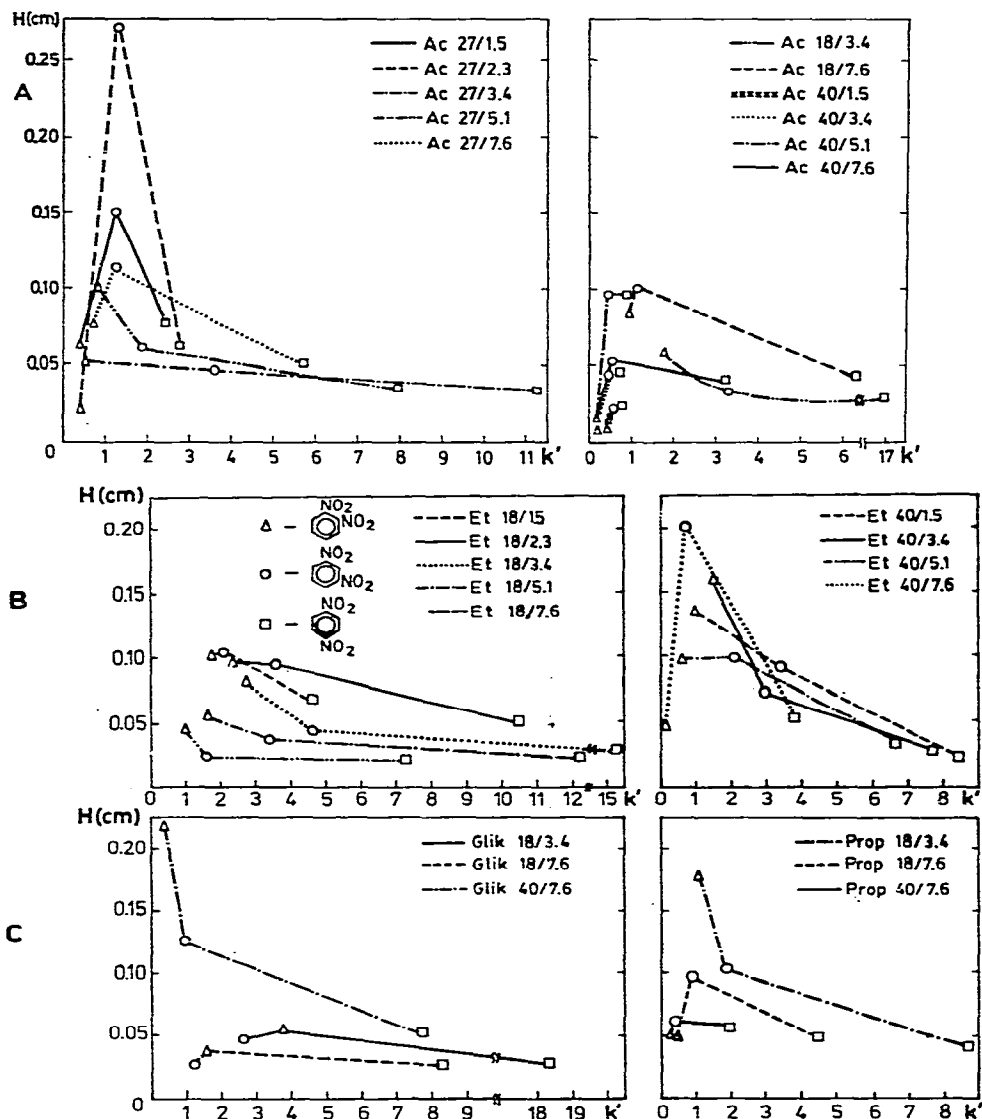


Fig. 1. Dependence of plate height ( $H$ ) on capacity factor ( $k'$ ) for  $\beta$ -Ni(NCS) $_2$ (4-MePy) $_4$  clathrate systems. Column: 40  $\times$  6 mm I.D.,  $d_p \approx 15 \mu\text{m}$ ; flow-rate, 10 ml/h. The clathrate sorbents were equilibrated with mobile phases containing as the organic solvents acetone (A), ethanol (B) and ethylene glycol (Glik) or *n*-propanol (Prop) (C).

height ( $H$ ) than  $C_{k,s}$  vary with changing particle size ( $d_p$ ) of the sorbent, and the relationship between  $H$  and  $d_p$  is complex (Fig. 3). Thus, a differentiation between the adsorption and absorption mechanisms mentioned above had to be based on indirect observations, namely that the rate of desorption of guest components from Ni(NCS) $_2$ (4-MePy) $_4$  clathrates to the gas phase is not limited by surface desorption<sup>6</sup>. In the following discussion we assume that the absorption mechanism is applicable.

If we suppose that the diffusion coefficients of the *ortho*, *meta* and *para* isomers of dinitrobenzene in the liquid phase may be regarded as equal to each other (to a

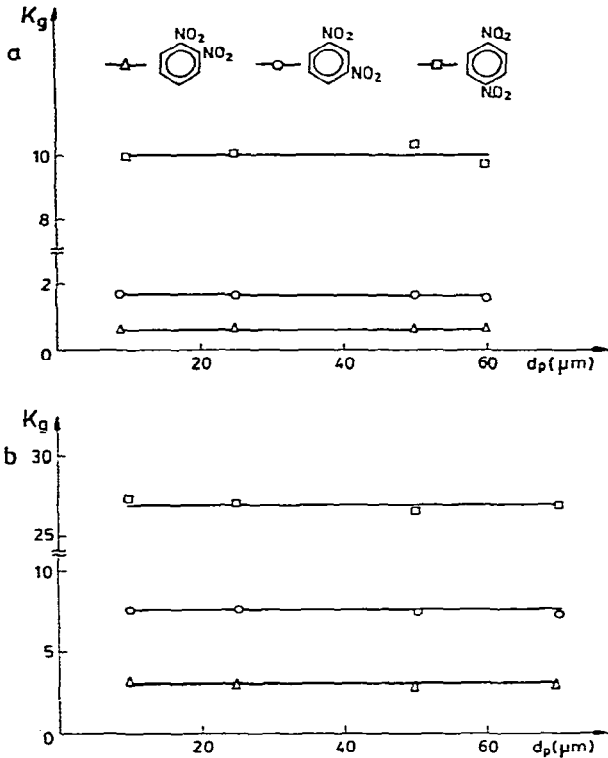


Fig. 2. Dependence of distribution coefficient ( $K_g$ ) on particle size ( $d_p$ ). Column:  $90 \times 5$  mm I.D.; flow-rate, 10 ml/h. Sorbents: a = Ac 27/7.6; b = Ac 27/3.4.

good approximation), the Giddings eqn. 1 may be rewritten, provided that the particle size and geometrical factors are constant

$$H = \text{const.} + C_{k,s} \cdot U \quad (4)$$

where  $\text{const.} = A + B/U + C_m \cdot U + C_k \cdot U$  and  $C_k$  is the adsorption-desorption contribution. Taking into account eqn. 2 and Einstein's diffusion equation

$$d^2 = 2t_d \cdot D_s \quad (5)$$

where  $d$  is the distance of diffusion and  $D_s$  the diffusion coefficient in the stationary phase, we obtain:

$$C_s = q \cdot \frac{d^2}{2D_s} \cdot \frac{k'}{(1+k')^2} \quad (6)$$

As is assumed above, the clathration-absorption process involves the whole volume of the clathrate particles. Thus we can set  $d = d_p$  and obtain:

$$H = \text{const.} + q \cdot d_p^2 \cdot U \cdot \frac{1}{2D_s} \cdot \frac{k'}{(1+k')^2} \quad (7)$$

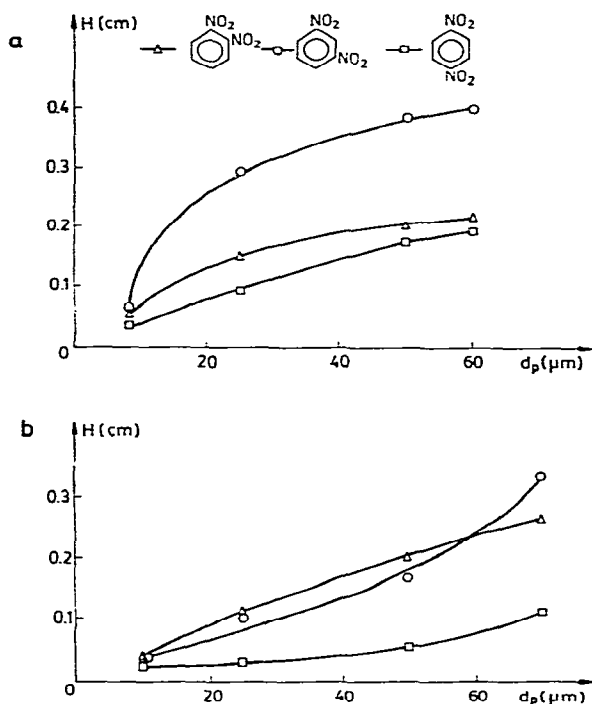


Fig. 3. Dependence of plate height ( $H$ ) on particle size ( $d_p$ ). Column:  $60 \times 5$  mm I.D.; flow-rate, 10 ml/h. Sorbents as in Fig. 2.

On the basis of eqn. 7 and determined values of  $H$  and  $k'$ , the coefficients of diffusion ( $D_s$ ) of the three dinitrobenzene isomers in the clathrate may be compared. The results are summarized in Table I. The most obvious effect is the difference between the diffusion coefficients of the *para* isomer and the two other isomers when dilatation of clathrate (sorbent) structure occurs. This result may be ascribed to a change in diffusion mechanism. Thus, when the channels are narrow (low  $V_{\text{mol}}$  values) the *para* isomer can penetrate the sorbent structure better than the other two isomers because of its "linear" Van der Waals molecular shape. On the other hand, dilatation of the structure may lead to better fitting of guest and cage in the clathrate. In such a case breaking of bonds between the cage and guest molecule rather than diffusion may become the rate determining step<sup>6</sup>. The results given in the Table I indicate that *p*-DNB fits the cages well when the molar volume of the clathrate is greater than 500 ml, the mechanism of diffusion of *p*-DNB changes and diffusion of *p*-DNB becomes slower.

To check the above considerations we can compare the molecular dimensions of *o*-, *m*- and *p*-DNB to the sizes of channels and cages in the  $\beta$ -structure. De Gil and Kerr<sup>3</sup> give the minimum channel apertures in  $\beta\text{-Ni}(\text{NCS})_2(4\text{-MePy})_4$  as  $3.3 \times 6.8 \text{ \AA}$ . Taking into account dilatation and contraction effects, the channel dimensions in the sorbents studied here are  $3.0\text{--}3.5 \times 6.2\text{--}7.0 \text{ \AA}$ . If one compares the limiting cross-section of the clathrate with the molecular dimensions of the DNB isomers (*p*-DNB  $3.4 \times 5.8 \times 9.8 \text{ \AA}$ , *m*-DNB  $3.4 \times 8.0 \times 8.0 \text{ \AA}$ , *o*-DNB  $3.4 \times 8.0 \times 8.0 \text{ \AA}$ ) it is obvious that only the *para* isomer is not sterically hindered

TABLE I

VARIATIONS OF DIFFUSION COEFFICIENTS ( $D_s$ ) OF DNB ISOMERS WITH MOLAR VOLUME ( $V_{mol}$ ) OF  $\beta$ -Ni(NCS)<sub>2</sub>(4-MePy)<sub>4</sub> CLATHRATE

Sorbent	$V_{mol}$	$D_s$
Ac 18/1.5	505.8	
Ac 18/3.4	514.4	$D_s(ortho) \approx D_s(meta) > D_s(para)$
Ac 18/7.6	520.6	
Ac 27/1.5	481.0	
Ac 27/2.3	487.9	$D_s(para) \gg D_s(meta)^*$
Ac 27/3.4	504.6	
Ac 27/5.1	516.7	$D_s(ortho) \approx D_s(meta) > D_s(para)$
Ac 27/7.6	517.4	
Ac 40/1.5	479.7	
Ac 40/3.4	491.0	$D_s(para) \gg D_s(meta)^*$
Ac 40/5.1	505.7	
Ac 40/7.6	512.3	$D_s(ortho) > D_s(meta) > D_s(para)$
Et 18/1.5	511.6	$D_s(meta) \approx D_s(para) > D_s(ortho)$
Et 18/3.4	520.1	$D_s(meta) \approx D_s(ortho) > D_s(para)$
Et 18/7.6	519.6	$D_s(meta) \approx D_s(ortho) > D_s(para)$
Et 40/1.5	500.4	$D_s(para) \gg D_s(ortho) > D_s(meta)$
Et 40/3.4	509.1	$D_s(para) \gg D_s(ortho) \approx D_s(meta)$
Et 40/7.6	512.3	$D_s(para) > D_s(ortho) \approx D_s(meta)$

\* The  $D_s$  value of the *ortho* isomers was neglected because of large extra-column effects for *o*-DNB ( $V_{R_{ortho}} \approx 1$  ml,  $V_o = 0.8$  ml).

and can pass through the channels, provided that the channels are expanded to dimensions of  $3.4 \times 5.8$  Å.

The literature data on the enthalpy<sup>4,5</sup> and selectivity<sup>9-11</sup> of clathration of isomers by the Ni(NCS)<sub>2</sub>(4-MePy)<sub>4</sub> complex are consistent with the above conclusions. *Para*-disubstituted benzene derivatives are preferably retained by the  $\beta$ -structure having  $V_{mol} > 500$  cm<sup>3</sup>, so the breaking of guest-cage interactions should require more energy in the case of clathrated *para* isomer than for the other two isomers. It may be concluded that:

(i) If the molar volume of the clathrate is relatively small (narrow channels) the diffusion rate is determined mainly by steric hindrances and that the narrow *para* isomer has a greater ability to pass through the channels than the wider *ortho* and *meta* isomers and the diffusion coefficients lie in the order  $D_s(para) > D_s(ortho) \approx D_s(meta)$ .

(ii) If the  $\beta$ -structure swells to a relatively large molar volume and the reaction of breaking of the guest-cage interactions is predominant in limiting the diffusion rate, the diffusion coefficient values lie in the order  $D_s(ortho) \approx D_s(meta) > D_s(para)$ .

It follows that diffusion inside the solid clathrate is, most probably, the slowest, and therefore rate determining step in the chromatographic separations studied in this work. The significance of these conclusions is related to the design of optimum conditions for chromatographic separations when using porous crystals, *i.e.*, clathrates of MeX<sub>2</sub>A<sub>4</sub> Werner complexes (where Me = Ni<sup>2+</sup>, Co<sup>2+</sup>, Fe<sup>2+</sup>, Mn<sup>2+</sup>; X = NCS<sup>-</sup>, NCO<sup>-</sup>; A = pyridine derivatives), as stationary phases.

TABLE II

DEPENDENCE OF RESOLUTION ( $R_s$ ) ON PARTICLE SIZE ( $d_p$ ) AND COLUMN LENGTH ( $L$ )

Column 5 mm I.D.;  $U = 10$  ml/h.  $R_s(o, m)$  represents the degree of separation of the *o*- and *m*-DNB isomers,  $R_s(m, p)$  that of the *m*- and *p*-DNB isomers.

Sorbent	Particle size ( $\mu\text{m}$ )	$R_s(o, m)$			$R_s(m, p)$		
		$L = 3$ cm	$L = 6$ cm	$L = 9$ cm	$L = 3$ cm	$L = 6$ cm	$L = 9$ cm
Ac 27/7.6	$8 \pm 2$	0.90	0.98	1.29	2.54	3.58	4.00
	$25 \pm 6$	0.40	0.40	0.80	1.28	1.92	2.56
	$50 \pm 10$	0	0.40	0.51	1.09	1.48	1.76
	$60 \pm 15$	0	0.40	0.39	0.92	1.38	1.67
Ac 27/3.4	$10 \pm 2$	1.40	1.86	2.16	2.65	4.47	5.03
	$25 \pm 5$	0.76	1.03	1.65	1.61	3.41	3.98
	$50 \pm 10$	<0.50	0.85	1.19	1.18	1.94	2.92
	$70 \pm 16$	<0.50	0.63	0.89	0.77	1.58	2.01

#### Optimization of operating parameters

Two sorbents were chosen: Ac 27/3.4,  $V_{\text{mol}} = 504.6$  ml; Ac 27/7.6,  $V_{\text{mol}} = 517.4$  ml.

**Effect of particle size.** Table II lists the resolution ( $R_s$ ) as a function of particle size and column length. Fig. 4 shows chromatographic separations using clathrate sorbents of various particle sizes. A considerable loss in efficiency of separation is ob-

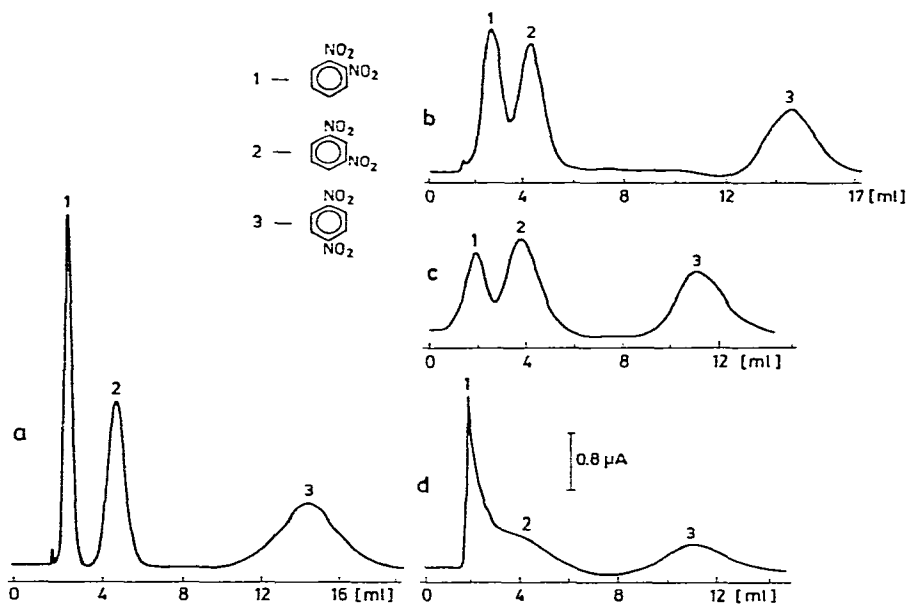


Fig. 4. Chromatographic separation of DNB isomers as a function of particle size ( $d_p$ ). Column as in Fig. 3. Sorbent Ac 27/3.4.  $d_p = 10 \pm 2 \mu\text{m}$  (a),  $25 \pm 5 \mu\text{m}$  (b),  $50 \pm 10 \mu\text{m}$  (c) and  $70 \pm 16 \mu\text{m}$  (d).



served when going to larger particle sizes, even at the level of  $25\ \mu\text{m}$ . Satisfactory separations require fine clathrate particles, of  $d_p \leq 10\ \mu\text{m}$ . In our experience, very fine clathrate crystals, smaller than *ca.*  $1\ \mu\text{m}$ , are not stable in contact with the liquid phase and recrystallize as larger crystals. In practice,  $5\ \mu\text{m} \leq d_p \leq 10\ \mu\text{m}$  is the range of utilizable particle size. The packing of a column with very fine particles also presents problems.

*Effect of column length.* According to theory, the resolution ( $R_s$ ) is proportional to the column length ( $L$ ). With long columns better separations are possible but the time of analysis increases. Fig. 5 shows the separation of DNB isomers obtained using columns of 3 cm and 9 cm length. The resolution of *o*- and *m*-DNB in a 9-cm column filled with  $25\text{-}\mu\text{m}$  particles is practically the same as in a 3-cm column of  $10\text{-}\mu\text{m}$  particles (see also Table II). However, the analysis time in the first case is about three times longer. So, taking into account the great selectivity of clathrate systems, it is advantageous in clathrate chromatography to use a short column (3–4 cm) of properly packed fine crystals.

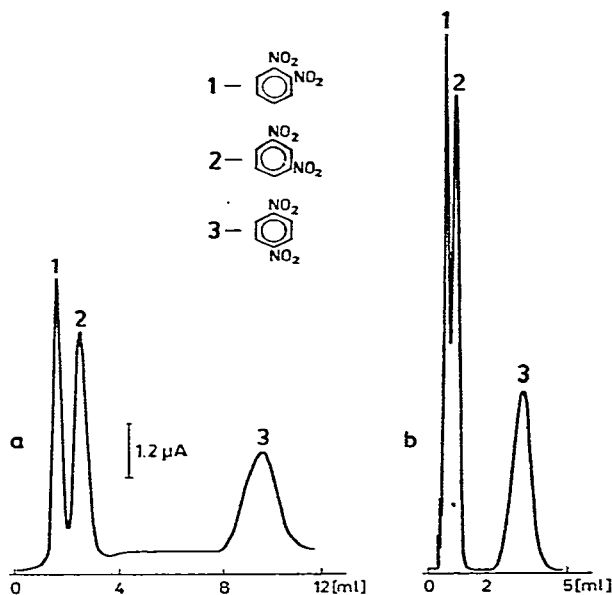


Fig. 5. Chromatographic separation of DNB isomers as a function of column length ( $L$ ). Column: 5 mm I.D.;  $d_p = 8\ \mu\text{m}$ .  $U = 10\ \text{ml/h}$ . Sorbent Ac 27/7.6.  $L = 9\ \text{cm}$  (a) and  $3\ \text{cm}$  (b).

*Effect of flow-rate.* The relationship between flow-rate ( $U$ ) and plate height ( $H$ ) is illustrated in Fig. 6. A characteristic feature is a minimum  $H$  value, and consequently a maximum of  $R_s$ , at a flow-rate value depending on the particle size. The range of optimum mobile phase flow-rates is rather narrow (4–6 ml/h) for  $d_p = 25\ \mu\text{m}$ . For  $U$  values lower than 4 ml/h, longitudinal diffusion contributes greatly to the peak broadening and at  $U > 6\ \text{ml/h}$ , according to the Giddings equation,  $H$  sharply increases with increasing  $U$ . In both these cases a significant loss in the column efficiency may be observed, so at  $U > 10\ \text{ml/h}$  the chromatographic separation is not satisfactory.

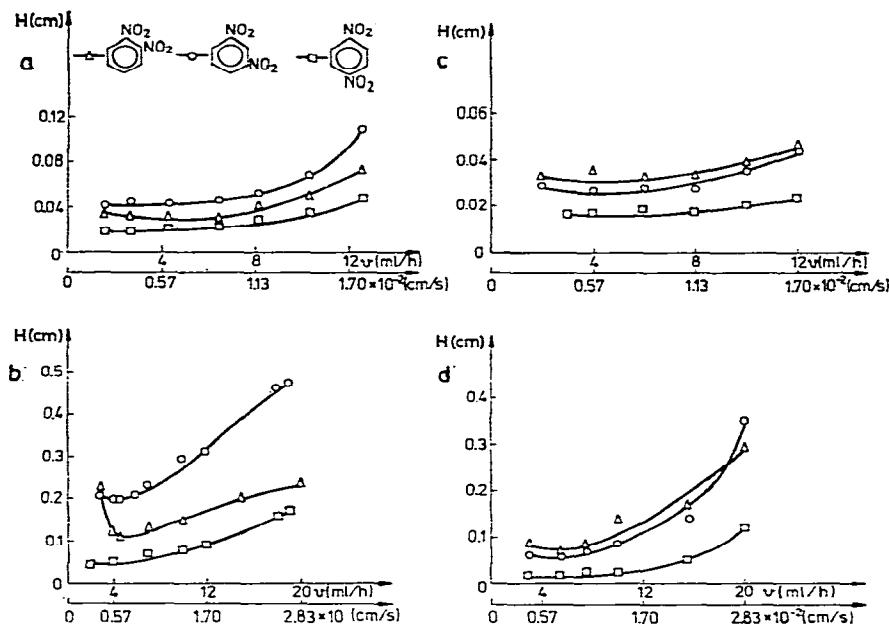


Fig. 6. Dependence of plate height ( $H$ ) on flow-rate ( $U$ ). Column:  $60 \times 5$  mm I.D. a, Sorbent Ac 27/7.6;  $d_p = 8 \pm 2 \mu\text{m}$ ; b, sorbent Ac 27/7.6,  $d_p = 25 \pm 6 \mu\text{m}$ ; c, sorbent Ac 27/3.4,  $d_p = 10 \pm 2 \mu\text{m}$ ; d, sorbent Ac 27/3.4,  $d_p = 25 \pm 5 \mu\text{m}$ .

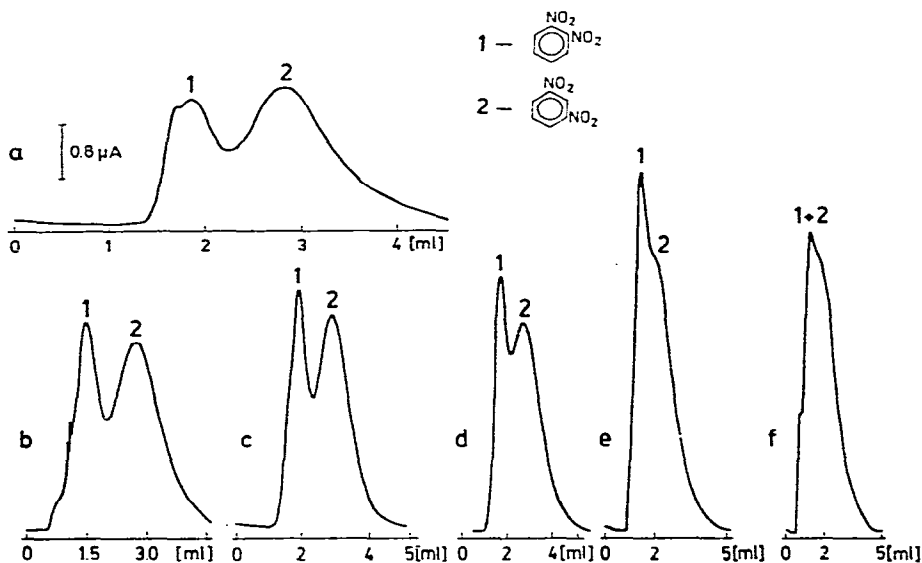


Fig. 7. Chromatographic separation of *o*- and *m*-DNB as a function of flow rate ( $U$ ). Column:  $60 \times 5$  mm I.D.;  $d_p = 25 \mu\text{m}$  Sorbent Ac 27/7.6. a,  $U = 3$  ml/h,  $R_s = 0.69$ ; b,  $U = 4.5$  ml/h,  $R_s = 0.77$ ; c,  $U = 7.5$  ml/h,  $R_s = 0.73$ ; d,  $U = 9$  ml/h,  $R_s = 0.61$ ; e,  $U = 20$  ml/h;  $R_s = 0.47$ ; f,  $U = 25$  ml/h,  $R_s = 0.41$ .

The variations in the separation with the flow-rate are shown in Fig. 7. The separation for  $d_p \approx 10 \mu\text{m}$  is less sharp than that for  $d_p = 25 \mu\text{m}$ . The optimum velocity range is 4–8 ml/h but a larger velocity than  $U_{\text{opt}}$  can be employed to provide faster separations without significant loss of column efficiency.

## CONCLUSIONS

The  $H$  values determined in this study are relatively high, as can be seen from the comparison given:

Liquid–solid adsorption chromatography <sup>12</sup>	$H = 0.05 \text{ cm}$
Liquid–liquid chromatography <sup>13</sup>	$H = 0.01 \text{ cm}$
Ion-exchange chromatography <sup>14</sup>	$H = 0.03 \text{ cm}$
Gel chromatography <sup>15</sup>	$H = 0.03\text{--}0.05 \text{ cm}$
Clathrate chromatography	$H = 0.1\text{--}0.3 \text{ cm}$ ( $U > 0.1 \text{ cm/sec}$ )

The data listed above were obtained using similar operating parameters, namely particle sizes between  $20 \mu\text{m}$  and  $30 \mu\text{m}$  and flow-rates of  $U = 0.1 \text{ cm/sec}$ . These data suggest relatively slow transport processes in the clathrate solid phase. This disadvantage would not appear if the solid were of larger porosity compared to the dimensions of the sorbate molecules. As is shown above, the diffusion of *ortho* and *meta* isomers of DNB through the  $\beta\text{-Ni}(\text{NCS})_2(4\text{-MePy})_4 \cdot \text{G}$  phase is sterically hindered. By choosing another solid phase, of larger channel cross-sections,  $\beta\text{-Ni}(\text{NCS})_2(4\text{-vinylpyridine})_4$ <sup>16</sup>, one may expect easier diffusion of the sorbate through the channels and hence lower  $H$  values. On the other hand, it is obvious that molecules smaller than DNB could diffuse through the channels of  $\beta\text{-Ni}(\text{NCS})_2(4\text{-MePy})_4$  more easily.

It may be concluded that clathrates formed by  $\text{MeX}_2\text{A}_4$  complexes may be useful in some specific separation problems because of their very high selectivity. The optimization of the separation processes may be achieved in three steps:

selection of an appropriate solid phase of a given porosity; at present, this is limited by the small number of crystalline structures determined;

modification of the porosity of the solid phase through lattice dilatation or contraction as described in Parts I and II of the present study for the  $\beta\text{-Ni}(\text{NCS})_2(4\text{-MePy})_4$  structure;

optimization of operating parameters.

## ACKNOWLEDGEMENT

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