EFFECT OF CROSS-LINKING OF A SULPHONIC CATION-EXCHANGE RESIN AND EFFECT OF TEMPERATURE ON THE CHROMATOGRAPHIC SEPARATION OF ISOMERS OF DINITROBENZENE

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SUMMARY

The effect of resin cross-linking and temperature on the elution of the *o*-, *m*- and *p*-isomers of dinitrobenzene from a chromatographic column was investigated. It was found that longitudinal diffusion in the resin phase affects the total plate height.

An example of the separation of isomers of dinitrobenzene is described.

INTRODUCTION

Aromatic compounds are strongly sorbed on ion-exchange resins. The sorption of uncharged molecules by ion-exchange resins that differ in their degree of cross-linking[1] and the effect of resin cross-linking on ion-exchange separations[2–4] have been investigated previously. Various nitro-compounds, including isomers, have been separated by elution development on a sulphonic cation exchanger[5].

It seemed interesting, therefore, to study the effect of resin cross-linking on the chromatographic separation of organic compounds. This paper describes part of studies on the effect of resin cross-linking and temperature on the distribution and chromatographic separation of *o*-, *m*- and *p*-dinitrobenzene (DNB).

EXPERIMENTAL

Ion-exchange resins

Wofatit KPS (H⁺) of 4, 6, 8, 10 and 16% divinylbenzene (DVB) nominal cross-linking, containing sulphonic acid functional groups was used.

The air-dried resins were ground in a mortar and sieved, and the gradual sedimentation method from a suspension in water[6] was employed to separate particles of 200–400 mesh for column experiments.

The resins were treated in a column successively with 1 N hydrochloric acid and 1 N sodium chloride solution. After several such cycles, the cation exchanger was washed with ethanol and then with water. The resins were then air-dried and stored in the H⁺ form. Their water contents were determined by drying them in an oven at 105° to constant weight. The exchange capacity was determined[7] by adding exactly 200 ml of standard 0.1 N sodium hydroxide solution in 5% (w/w) sodium

TABLE I

PROPERTIES OF THE RESINS USED

% DVB	Exchange capacity (mequiv./g dry resin, H^+)	Maximum water content (g water/g dry resin, H^+)	Density of H^+ form
4	4.15	2.48	0.328
6	4.00	1.80	0.388
8	5.45	1.32	0.516
10	5.10	1.08	0.630
16	6.65	1.02	0.713

chloride solution to *ca.* 1 g of resin, weighed into a dry 250-ml erlenmeyer flask. After standing overnight in the stoppered flask, 50-ml aliquots of the supernatant solution were back-titrated with standard 0.1 N hydrochloric acid with phenolphthalein as indicator. 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 resins used are summarized in Table I.

Apparatus and procedure

The technique of chromato-polarography[8,9] was chosen to monitor the effluent from the thermostatted 7 × 65 mm glass column filled with ion exchanger. The flow-rate used in all instances was 0.4 ml/min. A de-aerated aqueous solution (10% acetone + 0.05 M sulphuric acid) was used as eluent[5]. Methanolic solutions of isomers of DNB ($1 \cdot 10^{-2} M$) were prepared, injected separately into the column and eluted at 15, 25, 35 and 50°. The amount of the isomers of DNB injected was $1.7 \cdot 10^{-6}$ g in a volume of 5 μl.

TABLE II

WEIGHT-DISTRIBUTION COEFFICIENTS (λ) FOR ISOMERS OF DINITROBENZENE

% DVB	DNB isomer	λ			
		15°	25°	35°	50°
4	p-	14.5	11.7	11.2	7.5
	m-	17.8	15.5	13.0	10.3
	o-	22.6	20.1	16.2	11.9
6	p-	12.8	10.9	7.7	6.8
	m-	15.2	12.6	9.5	8.1
	o-	18.0	16.2	12.3	9.1
8	p-	9.8	7.7	6.5	5.9
	m-	12.9	9.8	8.6	6.9
	o-	18.1	14.3	10.7	8.3
10	p-	7.1	5.8	5.3	6.0
	m-	8.9	7.4	6.4	7.0
	o-	11.7	9.1	7.9	8.3
16	p-	6.0	5.3	4.6	3.3
	m-	7.4	6.0	5.3	3.7
	o-	10.6	8.0	6.3	3.8
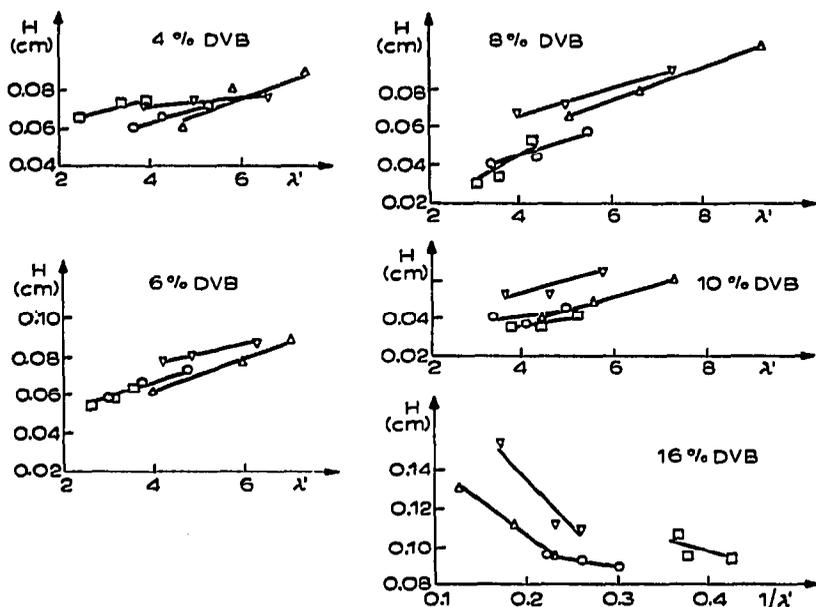
Fig. 1. Plate height (H) as a function of the bed distribution coefficient (λ'), and as a function of $1/\lambda'$ for resin of 16% DVB cross-linking. △, 15°; ▽, 25°; ○, 35°; □, 50°.

RESULTS

The weight distribution coefficients, λ (summarized in Table II), and experimental plate heights were calculated[10] from the elution curves.

Plate heights, H, are plotted as a function of the bed distribution coefficient, λ', where, $\lambda' = \lambda \cdot d_z$, in Fig. 1. It can be seen that there is almost strictly linear de-
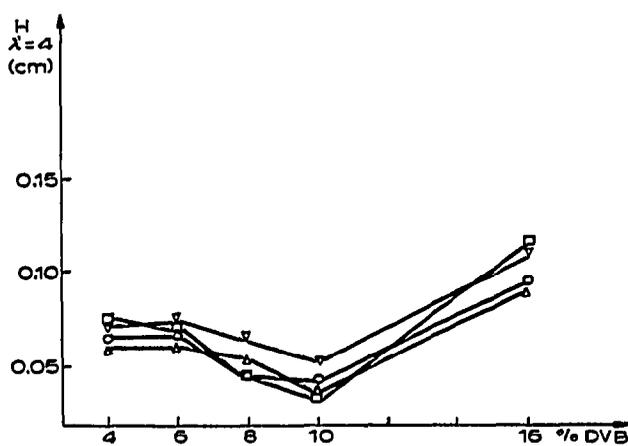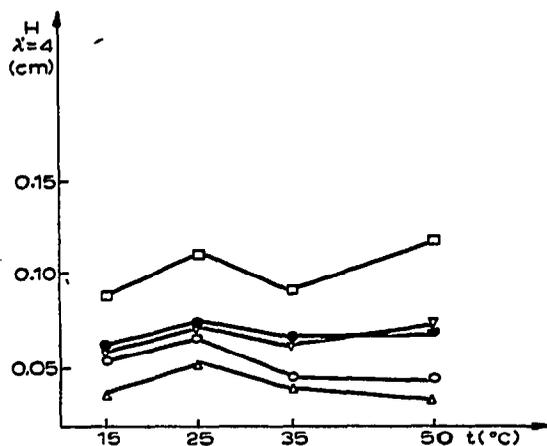
Fig. 2. Plate height ($H_{\lambda'=4}$), normalized for a bed distribution coefficient of 4, as a function of temperature. ▽, 4% DVB; ●, 6% DVB; ○, 8% DVB; △, 10% DVB; □, 16% DVB.

Fig. 3. Plate height ($H_{\lambda'=4}$), normalized for a bed distribution coefficient of 4, as a function of the degree of cross-linking. △, 15°; ▽, 25°; ○, 35°; □, 50°.

pendence between H and λ' for resins of 4, 6, 8 and 10% DVB cross-linking, and also between H and $1/\lambda'$ for the resin of 16% DVB cross-linking. Plate heights, normalized for a bed distribution coefficient of 4 by extrapolating the linear dependences, are plotted as a function of temperature in Fig. 2 and as a function of the degree of cross-linking in Fig. 3.

DISCUSSION

It has been found, that the sorption of dinitrobenzenes is less at higher temperatures for all the degrees of cross-linking examined. The weight-distribution coefficients tend to decrease with increasing degree of cross-linking at all temperatures.

The plate height, H, changes slightly with increase in temperature for three isomers, independent of the resin cross-linking. In most instances, H tends to decrease. For all elution temperatures, H decreases with a decrease in the bed distribution coefficient (cf., Fig. 1), which may be a reason for the tendency of the plate height to decrease with increasing temperature.

The plate height, normalized for a bed distribution coefficient of 4, depends less on the increase in temperature in comparison with the effect of cross-linking (cf., Figs. 2 and 3). The changes in the normalized plate height with temperature can be neglected. For all elution temperatures, H decreases with the increase in the degree of cross-linking up to 10% DVB, where a minimum was observed, and H subsequently increases with further increase in the degree of cross-linking up to 16% DVB.

The origin of the changes in plate height with resin cross-linking in the system examined is of interest. The shape of the $H\lambda'_{=4}$ versus % DVB plot can be explained by the theoretical equation for the plate height in ion-exchange chromatography[3,4]:

$$H = A + \frac{B}{\bar{D}} + C + E + F \cdot \bar{D} \tag{1}$$

where A, B, C, E and F are constants under particular experimental conditions and $\bar{D}$ is the diffusion coefficient. Diffusion coefficients of isomers of DNB in the resin phase are not available, but usually diffusion coefficients decrease with an increase in the degree of cross-linking[11]. Assuming that the diffusion coefficients decrease approximately linearly with an increase in the degree of cross-linking and the diffusional mass transfer in the resin phase (the second and fifth terms on the right-hand side of eqn. 1) is the main factor determining the plate height, it is easy to conclude that when $\bar{D}$ decreases with an increase in the degree of cross-linking from 4% to 10% DVB, the significant contribution of longitudinal diffusion in the stationary phase for the less cross-linked resins is the reason why the plate height decreases. For Wofatit KPS of 10% DVB, a minimum occurs and $\bar{D} = \sqrt{B/F}$. A further decrease in $\bar{D}$ with increase in the degree of cross-linking up to 16% DVB indicates that the second term must be operative and must be a reason for the increase in the plate height.

Such an explanation of the H versus % DVB dependence seems to be reasonable, although it is possible that the effect of differences in particle size distribution in the broad range of mesh size used (200–400 mesh) may interfere. After consider-
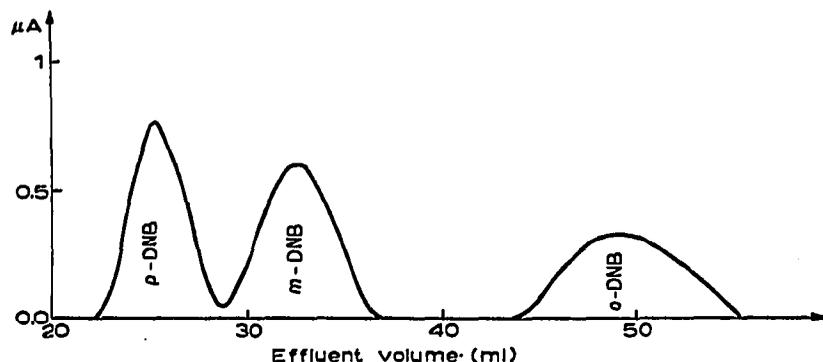
Fig. 4. Separation of the isomers of dinitrobenzene. Wofatit KPS of 8% DVB (7 × 300 mm) column. Eluent, 10% acetone + 0.05 M H_2SO_4. Flow-rate, 0.4 ml/min. Temperature, 30°. Ordinate, intensity of the reduction current.

ation of the dependence of the calculated resolution[10] on the degree of cross-linking and on temperature, the resin of 8% DVB nominal cross-linking and a temperature of 30° were chosen for the separation, and the isomers of DNB were separated (Fig. 4).

REFERENCES

1 D. Reichenberg and W. F. Wall, *J. Chem. Soc.*, (1956) 3364.
2 R. Dybczyński, Institute of Nuclear Research, Report No. 1115 (VIII) C, 1969.
3 R. Dybczyński, *J. Chromatogr.*, 50 (1970) 487.
4 R. Dybczyński, *J. Chromatogr.*, 71 (1972) 507.
5 W. Kemula and S. Brzozowski, *Rocz. Chem.*, 35 (1961) 711.
6 J. Minczewski and R. Dybczyński, *J. Chromatogr.*, 7 (1962) 98.
7 P. Helfferich, *Ion Exchange*, McGraw-Hill, New York, 1962, p. 91.
8 W. Kemula, *Rocz. Chem.*, 26 (1952) 281.
9 W. Kemula, in *Progress in Polarography*, Vol. 2, Wiley-Interscience, New York, 1962, p. 397.
10 R. Dybczyński, *J. Chromatogr.*, 31 (1967) 155.
11 G. E. Boyd, B. A. Soldano, *J. Amer. Chem. Soc.*, 75 (1953) 6091.