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Note

Separation of urea–formaldehyde addition products by gel permeation chromatography

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In basic media, urea and formaldehyde undergo reaction to produce, primarily, a range of methylol-substituted urea derivatives:

$$NH_2\text{–}CO\text{–}NH_2 + CH_2O \rightleftharpoons NH_2\text{–}CO\text{–}NHCH_2OH \quad \text{Monomethylolurea}$$

$$\Big\Vert\ CH_2O$$

$$HOCH_2NHCON(CH_2OH)_2 \xleftarrow{CH_2O} CO(NHCH_2OH)_2 \quad \text{Dimethylolurea}$$

Trimethylolurea

This reaction sequence is the first step involved in the production of urea–formaldehyde resins.

The reaction course has been studied elsewhere by a number of methods, including volumetric analysis[1], paper chromatography[2], gas–liquid chromatography[3] and ^{13}C nuclear magnetic resonance[4]. In this paper, we have used gel permeation chromatography to separate and identify four of the major species involved in the reaction, *viz.*, urea, formaldehyde, monomethylolurea and dimethylolurea. No experiments could be carried out with trimethylolurea, since it has not yet been possible to isolate the pure compound.

EXPERIMENTAL

Materials

The separation media studied were: (a) Enzacryl Gel KO (extra fine), a N-acryloylmorpholine and N,N′-methylenediacrylamide copolymer supplied by Koch-Light Labs. (Colnbrook, Great Britain) of particle size $<45\ \mu m$; and (b) Sephadex G-10, a cross-linked dextran gel supplied by Pharmacia (Uppsala, Sweden). The particle size of Sephadex G-10 as delivered is 40–120 μm, but this was dry-sieved and only particles of size $<63\ \mu m$ were used.

The urea and formalin (37%, w/v, aq. solution) employed were standard Analar-grade reagents. Both the monomethylolurea and dimethylolourea were pre-

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pared in the laboratory by established methods[5]. In all experiments, the solvent and eluent employed was de-aerated de-ionised water.

Apparatus

For both gels, two 100 cm × 4 mm I.D. glass columns equipped with water jackets were used. Both column pairs were connected in series, with a sample-injection head connected at the column input. The flow-rate was controlled by a positive-displacement metering pump (Dosapro-Milton Roy Instrument Minipump) and the column eluent was monitored by a differential refractometer (Waters Assoc. Model R401).

Procedure

The gels were packed in the columns by use of extension tubes[6]. After removal of the loading funnel, the columns were conditioned by pumping solvent through at approximately twice the projected flow-rate; when the bed had ceased to pack under these conditions, the extension tube was removed. The column pairs were coupled in series with a small length of PTFE tubing.

After equilibrating each pair of columns, the void volume (V_0) and the totally accessible liquid volume (V_S) were determined by eluting Blue Dextran and deuterium oxide at the desired flow-rate.

In all experiments, 40-μl samples were injected on to the columns, and elution conditions were chosen to give optimum resolution. On both columns, chromatograms of urea, monomethylolurea, dimethylolurea and formalin were obtained for the pure compounds alone and in admixture with one another.

RESULTS AND DISCUSSION

Each experiment was carried out at the previously determined optimum operating conditions for the individual gels; this procedure was adopted in order to obtain the most efficient separation of the species possible for each gel type.

Enzacryl KO columns

Efficiency measurements of the packed columns gave a maximum value of 3200 theoretical plates per metre at a flow-rate of 2.3 $cm^3\ h^{-1}$.

Table I gives the distribution coefficients, K_d, for the species under study; these were calculated from chromatograms of pure samples.

TABLE I

DISTRIBUTION COEFFICIENTS OF MODEL COMPOUNDS

Compound	*Mol. Wt.*	*Enzacryl KO*	*Sephadex G-10*	
		K_d	K_d	R
Urea	60	1.11	1.11	2.05
Monomethylolurea	90	0.95	0.86	0.78
Formaldehyde	30	0.93	0.74	0.59
Dimethylolurea	120	0.74	0.66	—

The high K_d value for urea (1.11) indicates that some adsorption to the gel has occurred, probably via the free amino groups. This would also account for the relatively high value obtained for monomethylolurea.

Unfortunately, a consequence of this adsorption effect combined with the low column efficiency is the very close proximity in which formaldehyde (K_d 0.93) and monomethylolurea (K_d 0.95) are eluted. This resulted in there being no resolution whatsoever between these two species when in admixture. All the remaining compounds were, however, well resolved.

Although these columns could not resolve formaldehyde and monomethylolurea, it has been reported that all four species can be separated with a modified Enzacryl gel [a cross-linked poly(N-acrylolyl-L-prolylmorpholine)][7].

Sephadex G-10 columns

The column efficiency was calculated and found to be 4520 theoretical plates per metre at a flow-rate of 4.5 $cm^3\ h^{-1}$; Table I gives the K_d values obtained for the species under study.

Again, the K_d value for urea shows that an adsorption mechanism is operating, this being in agreement with previous results reported for Sephadex gels[8,9]. The peaks for urea and both substituted ureas are symmetrical, but the peak for formaldehyde exhibits considerable tailing; however, no undesirable reduction in resolution or sensitivity occurs. Chromatograms of all four species in admixture show good resolution (see Fig. 1).

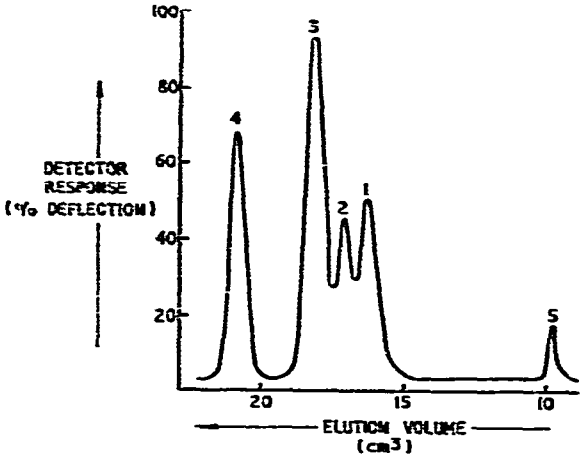

Fig. 1. Typical chromatogram from a Sephadex G-10 column. Peaks: 1 = dimethylolurea; 2 = formaldehyde; 3 = monomethylolurea; 4 = urea; 5 = blue dextran.

Table I also gives the resolution factors, R, calculated for adjacent peaks on the chromatogram.

Initial studies have been carried out on a range of urea–formaldehyde reaction mixtures in alkaline media; Fig. 2 shows a typical chromatogram obtained at pH 9 with a 1:2.5 molar ratio of urea to formaldehyde. As can be seen, although an as yet unidentified peak is present, no interference is encountered in the separation of the four species under study.

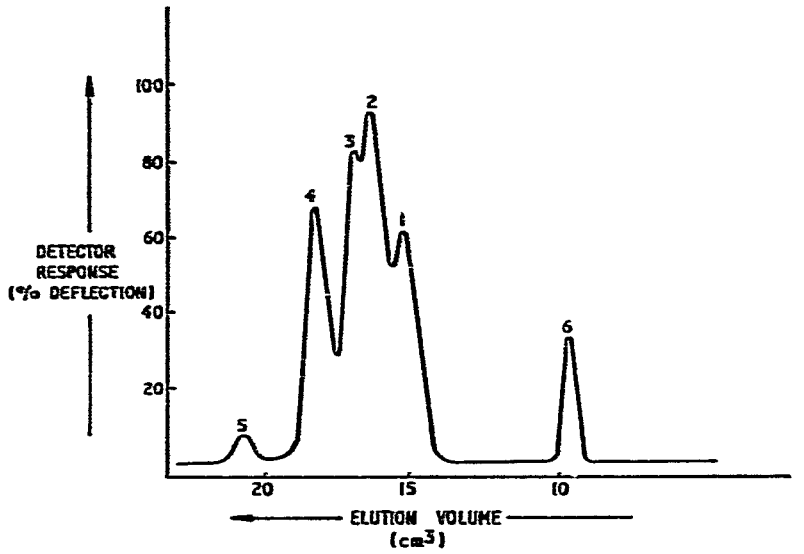

Fig. 2. Chromatogram of an actual urea–formaldehyde reaction mixture. Peaks: 1 = unknown; 2 = dimethylolurea; 3 = formaldehyde; 4 = monomethylolurea; 5 = urea; 6 = blue dextran.

CONCLUSION

All four compounds studied were successfully resolved from one another on Sephadex G-10 columns, despite having only incremental differences in molecular weight of 30.

With Enzacryl KO gel, only three compounds could be resolved; no resolution of formaldehyde and monomethylolurea could be achieved. This may have been due to the relatively low efficiency obtained with these columns (only 3200 theoretical plates per metre).

Adsorption of one or more of the compounds occurs with both gels, producing K_d values somewhat larger than expected. Results indicate that this adsorption occurs via the amino groups present, with free amino groups adsorbing more strongly than substituted ones.

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