

Note

Separation of methylol derivatives of imidazolidines, urea and carbamates by liquid chromatography

KEITH R. BECK and BEVERLY J. LEIBOWITZ

Department of Consumer Sciences and Retailing, Purdue University, West Lafayette, Ind. 47907 (U.S.A.)

and

MICHAEL R. LADISCH

Laboratory of Renewable Resources Engineering, Purdue University, West Lafayette, Ind. 47907 (U.S.A.)

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Agents used to crosslink cellulose and produce durable press cotton fabrics include bis(1,3-hydroxymethyl)4,5-dihydroxyimidazolidinone (I), hydroxymethyl derivatives of urea (II), carbamates (III), and other nitrogenous compounds (Fig. 1). Since 100 million pounds of these chemicals are used annually by the U.S.A. textile industry, the analysis for these water soluble compounds is of significant interest. Previously reported methods of analysis include gas chromatography (GC)¹, thin-layer chromatography (TLC)²⁻³, gel permeation chromatography (GPC)⁴ and nuclear magnetic resonance (NMR)⁵.

The polar character of durable press agents, together with their high solubility

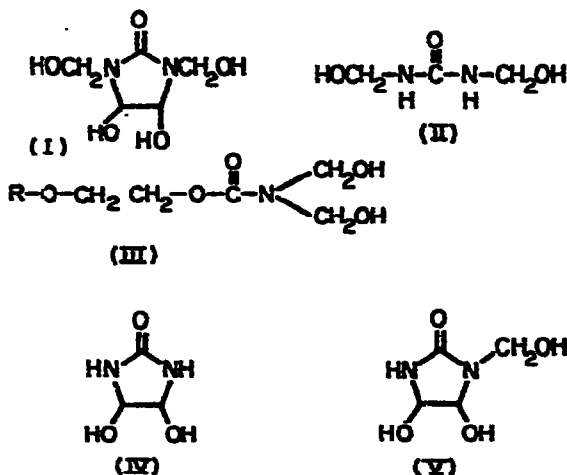


Fig. 1. Molecular structures of durable-press agents. (I) Bis(1,3-hydroxymethyl)4,5-dihydroxyimidazolidinone; (II) bis(1,3)hydroxymethyl urea; (III) bis(hydroxymethyl)carbamate; (IV) 4,5-dihydroxyimidazolidinone; and (V) 1-hydroxymethyl-4,5-dihydroxyimidazolidinone.

in water; suggested potential for aqueous liquid chromatography which has already been successfully applied to separation of carbohydrates⁶⁻¹⁰. Carbohydrates and durable press finishes are similar in that both have numerous heteroatoms and hydroxyl groups. This paper describes the separation of N-methylol compounds using Q-15S cation-exchange resin in the Li⁺ form with water as the sole eluent at relatively low operational pressures.

MATERIALS AND METHODS

Synthetic imidazolidinones were prepared as described elsewhere^{11,16}. Commercial durable press agents were donated by American Cyanamid (Aerotex), BASF (Ludwigshafen, G.F.R.) (carbamate U-4750) and Standard Chemical Co. (Stanset). Analytical samples were prepared by diluting the commercial samples one hundred fold to give concentrations of 4-6 mg/ml in water. The resin used was Aminex Q-15S (Bio-Rad Labs., Richmond, Calif., U.S.A.) which is a 6% sulfonated divinyl benzene crosslinked polystyrene analytical grade cation exchange resin of particle size $22 \pm 3 \mu\text{m}$.

The liquid chromatograph was constructed from several components manufactured or supplied by Laboratory Data Control (Riviera Beach, Fla., U.S.A.): a Rheodyne Model 7120 injector with a 20- μl injector loop, a Constametric IIG pump, a Gradient Master flow controller and a refractometer Model 1107 thermostated to 32° by a Haake Model FE circulating water bath (Saddlebrook, N.J., U.S.A.). Signals from the refractometer were recorded by a strip chart recorder and a Spectra-Physics minigrator (Santa Clara, Calif., U.S.A.).

The resin was packed in a 39 cm by 6 mm I.D. (9.5 mm O.D.) stainless-steel column fitted with 10- μm inlet and outlet end fittings (Waters Assoc.). The column was enclosed in a 20-mm I.D. glass jacket and thermostated with a Haake Model FE circulating water bath at constant temperatures ranging from 60-80°. Degassed water was prepared and used as described previously¹⁰.

Aminex Q-15S was converted to the lithium form and packed using the same procedure as described previously¹⁰ for AG-50W-X4 except lithium chloride replaced calcium chloride. Careful attention was given to removing resin fines¹⁰ and uniformity of particle size was verified prior to packing by scanning electron microscopy.

After packing, the column was connected to the liquid chromatograph and heated for 2 h to the desired temperature. Flow of degassed distilled water through the column was subsequently initiated over a 20-min period by gradually increasing the flow. Once started, water was pumped through the column at a constant flow-rate for 24 h per day during use. To assure that the water entering the column was degassed, the water was vigorously boiled for 15 min prior to filling the solvent reservoir. The water was then kept at 85-90° in the reservoir at all times. Typical operational pressure drop through columns of this sort was about 50-100 p.s.i.g.

Prior to using columns described in this paper, it was necessary to optimize column temperature and flow-rate. Chromatograms of a carbamate mixture (Stanset C-90) at various temperatures and flow-rates were used to calculate theoretical plates per meter (*N*) and the resolution factor (*R*) with peak widths (*PW*) were measured at 10% of peak height¹⁷. These runs indicated an optimum temperature of

60° and a maximum flow-rate of 0.5 ml/min or less (see Tables I and II). A flow-rate of 0.5 ml/min was selected.

At a column temperature of 60° and a flow-rate of 0.5 ml/min, calibration curves of peak height and area (Fig. 2) for DHEU (IV in Fig. 1), and Stanset FR,

TABLE I

EFFECT OF TEMPERATURE ON THEORETICAL PLATES PER METER (N) AND RESOLUTION FACTOR (R) FOR STANSET C-90

Flow-rate, 0.5 ml/min.

Temperature (°C)	N_A	N_B	R_{AB}
50.0	3876	2996	1.34
55.0	4396	3175	1.33
60.0	5428	3996	1.36
65.0	4433	3869	1.25
70.0	4167	3148	1.04

TABLE II

EFFECT OF FLOW ON THEORETICAL PLATES PER METER (N) AND RESOLUTION FACTOR (R) FOR STANSET C-90

Temperature, 60 °C.

Flow-rate (ml/min)	N_A	N_B	R_{AB}
0.30	6314	5661	1.54
0.35	5559	4845	1.43
0.40	5380	5090	1.49
0.45	4516	3715	1.33
0.50	5428	3996	1.36
0.55	4060	2863	1.17
0.60	2952	3029	1.09
0.65	4211	3148	1.20
0.70	4515	2570	1.10

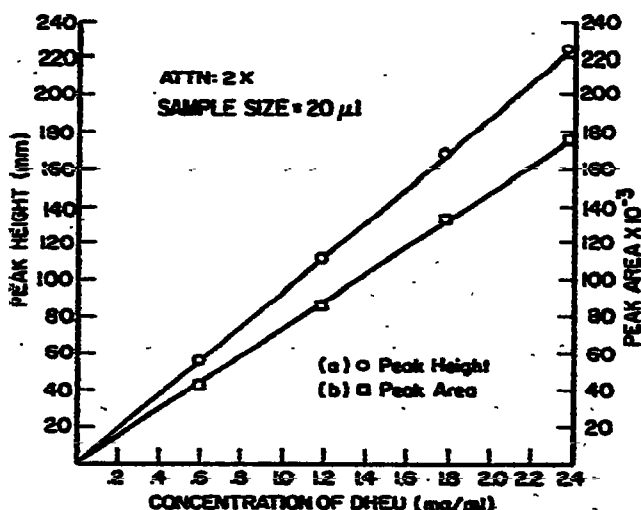


Fig. 2. Calibration curve based on (a) peak height and (b) peak area for DHEU (IV in Fig. 1).

the major component of which is DMDHEU (I in Fig. 1), were obtained. These plots show that detector and integrator responses are linear over a range of 0.04 to 2.5 mg/ml with a standard deviation of less than 2 mm for peak height and less than 2.5% of the area units. The detection limit under these conditions is 0.03 mg/ml (30 ppm).

RESULTS AND DISCUSSION

Reaction mixtures containing the reactants glyoxal and urea, the product 4,5-dihydroxy-2-imidazolidinone (IV in Fig. 1), ethanol and salts are readily separated. A chromatogram for the glyoxal-urea reaction is shown in Fig. 3. Good resolution is also obtained for the mixture of reactants and products arising from the reaction

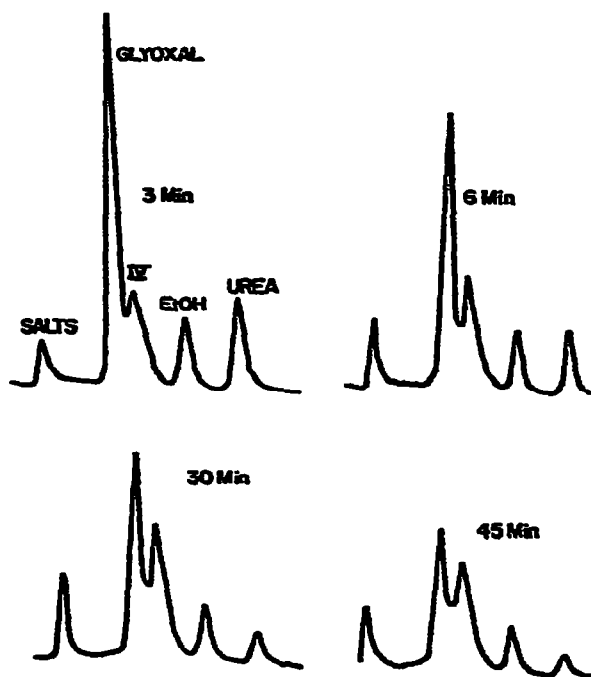


Fig. 3. Chromatogram of DHEU formation from glyoxal and urea.

between DHEU and formaldehyde (Fig. 4). This has applications to quality control and the study of reaction kinetics. In addition, the quantification of formaldehyde in the reaction mixture is important since the textile industry is attempting to control free formaldehyde in finish baths in view of its toxicological properties. The use of liquid chromatography (LC) for formaldehyde analysis could supplement existing titrimetric¹² or spectrophotometric analysis¹³.

Illustrations of analyses of some commercial durable-press finishing compositions are shown in Fig. 5. These samples were dissolved in water and injected directly without sample clean-up. It is apparent that the major component (11.0 min)

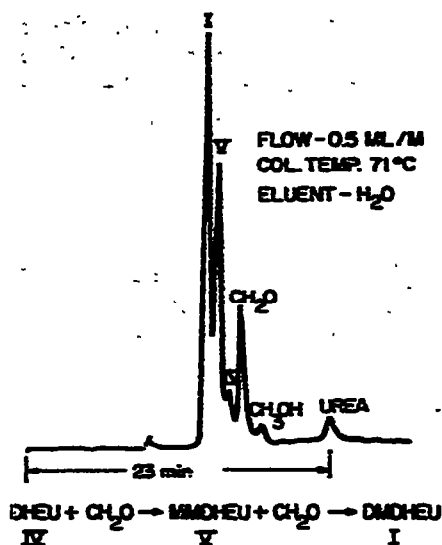


Fig. 4. Chromatogram of reactants and product in DMDHEU formation. Formaldehyde (CH₂O) is stabilized by methanol (MeOH) in original reactant mixture.

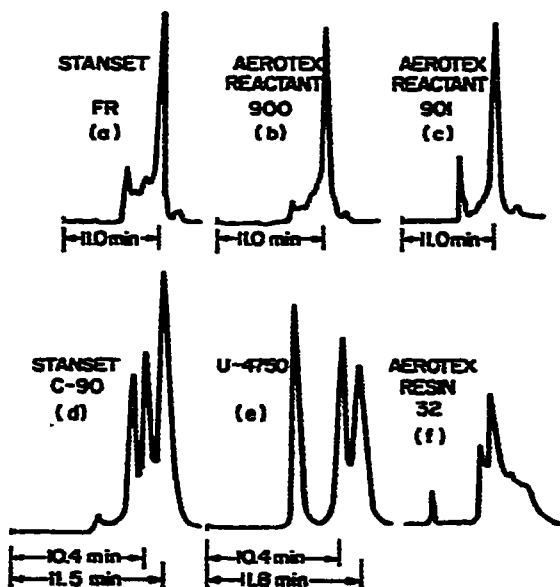


Fig. 5. Analysis of commercial durable-press agents. Imidazolidinones (a-c), carbamates (d-e); methyl urea (f).

in Fig. 5a, b and c is the same. This can be shown by comparison with synthetic authentic samples to be DMDHEU (I). Reactant 901 (c) is a buffered modification of Reactant 900 (b) as is apparent from the larger salt peak at the exclusion volume. Two different carbamate systems are shown in (d) and (e). From these chromatograms, it can be concluded that the last two peaks (11.5 and 11.8 min) are identical,

but are present in different proportions. The two components were not identified, but one is probably the dihydroxymethyl derivative of methoxyethylcarbamate (III, $R=CH_3$), since Stanset C-90 is described as a methoxyethylcarbamate. Aerotex Resin 52 (f) is a modified urea formaldehyde condensate. Since a variety of condensation products are possible, the chromatogram shows a smear rather than well-resolved peaks as in the other examples.

The selectivity for the various components in these samples is a function of the cation since, for example, resolution of the components in Fig. 5 is poor if the Ca^{2+} or Na^+ form of the resin is used instead of the Li^+ form. This effect has previously been discussed in terms of steric configurations for other (carbohydrate) components¹⁴. Additional explanation of the cation effect may be useful in the context of Pearson's classification of Lewis bases¹⁵.

According to this concept, Lewis bases are "hard" if the basic atom is small and fairly electronegative. If the basic atom is large and less electronegative, it is said to be soft, since its electron cloud is more easily distorted. Oxygen and nitrogen are both hard bases under the classification scheme. Pearson's theory also states that hard bases interact best with hard acids and soft bases interact best with soft acids.

Compounds I-V all contain N and O atoms with unshared pairs of electrons and therefore are Lewis bases. With these considerations in mind, three ions of increasing hardness (Ca^{2+} , Na^+ and Li^+ , respectively) were selected for investigation. Columns of the appropriate ionic form were packed and tested. Of the three forms, the Li^+ column gave the best results. This preliminary work suggests that the hardness of the ion may affect column performance. In other words, Li^+ , being a hard acid complexes with durable press agents which are hard bases when taken in the context of Pearson's theory. Of course, other factors besides "hardness/softness" effects, such as exclusion and hydrogen bonding effects would also be expected to play a role. Further study is needed to elucidate the role of these effects relative to column performance.

CONCLUSIONS

LC is capable of separating selected polar durable press agents. This separation is of interest not only for its potential application to textile finish research and quality control, but also as another means of carrying out further studies on the mechanism of separation on ion-exchange resins in aqueous environments.

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