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USE OF REVERSED-PHASE HIGH-PERFORMANCE LIQUID CHROMATOGRAPHY IN CHARACTERIZATIONS OF REACTANTS IN DURABLE-PRESS FINISHING OF COTTON FABRICS*

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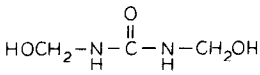
SUMMARY

The principal class of reactants used to impart durable-press properties to cotton fabrics is methylolamides. These properties are obtained by etherification of the cotton cellulose hydroxyls through a carbocation mechanism. Through use of reversed-phase high-performance liquid chromatography, with water as the mobile phase and a refractive index detector, the initial methylol populations of representative reactants were established. As the amount of formaldehyde in a reactant is increased, the ratio of monomethylol derivative to polymethylol derivatives is decreased. Responses of the populations to hydrolysis and catalyst conditions were studied. These conditions result in the emergence of peaks representative of condensations and byproducts to the simple methylolation reactions. Comparisons of results with those from ^{1}H and ^{13}C nuclear magnetic resonance analyses are described.

INTRODUCTION

The principal class of reactants to impart durable-press or smooth-drying properties to cotton-containing textiles is methylolamides and their derivatives[1]. The methylolation takes place by reaction of a di- or polyfunctional amide with formaldehyde. Examples of possible reaction products are dimethylolurea, from reaction of formaldehyde with urea:



and dimethyloldihydroxyethyleneurea (DMDHEU), from reaction of formaldehyde

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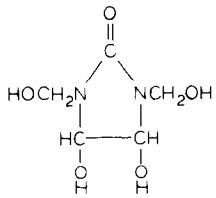
with dihydroxyethyleneurea:



The formation of DMDHEU has been followed by reversed-phase high-performance liquid chromatography (HPLC) with an ion exchange column by Beck *et al.*[2]. Kantschev and Nesnakomova have followed the preparation of the intermediate, 4,5-dihydroxyethyleneurea, from urea and glyoxal, with thin-layer chromatography[3]. The mechanisms for these reactions, and for the formation of cellulose cross-links or of etherified methylolamides through a carbocation mechanism, have been established by hydrolysis studies[4–6].

Although single product formation was presumed in most cases, the reactions of both etherification and methylolation are reversible to produce a methylolamide (I) and free amide and formaldehyde (II) (Fig. 1).

Equilibria exist both for the methylolated amides with the free amide and formaldehyde, and for the ether with the alcohol and methylolamides[7,8]. Therefore, any system involving a methylolamide cross-linking agent contains an equilibrium mixture of starting materials and reaction products, and the chromatography is that of an equilibrium system.

EXPERIMENTAL

Materials

Urea, glyoxal, glyoxylic acid, glycolic acid, oxalic acid, acetylenediurea, hydantoin, formaldehyde as formalin, and zinc nitrate hexahydrate were reagent grade chemicals. Dihydroxyethyleneurea (DHEU), m.p. 132–134°C, was prepared from urea and glyoxal according to known methods[9]. The methylolated derivatives of urea, dihydroxyethyleneurea, acetylenediurea and hydantoin were non-isolated compounds prepared by reaction of the amide with formaldehyde at the optimum pH of methylolation for each derivative, in the mole ratios indicated in the tables. Partially etherified derivatives of the methylolated compounds also were not isolated. 4,5-

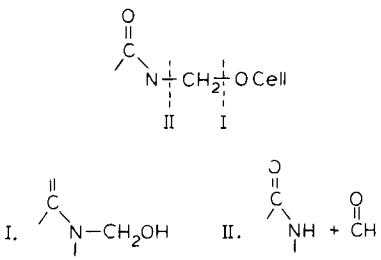


Fig. 1. Sites for cleavage in amidomethyl ether of cellulose to form methylolamide (I) and free amide and formaldehyde (II).

Dimethoxy-1,3-bis(methoxymethyl)ethyleneurea, 4,5-dimethoxy-1-methyl-3-methoxymethyl-ethyleneurea and 4,5-dimethoxyethyleneurea were isolated compounds furnished by Dr. Harro Petersen, Ammonia Laboratory, BASF, Ludwigshafen am Rhein, F.R.G.*.

Chromatography

Separations were performed on a Waters 10-μm μBondapak C_{18} column. A Waters liquid chromatograph was equipped with a M6000A pump, a U6K syringe injector and a RI detector. Reversed-phase HPLC was used with water as the mobile phase unless otherwise indicated. Injections were 10 μl of either 2% solutions (equilibrium mixtures) or 0.5% solutions (isolated compounds). The internal standard method of identification was used where possible. Either peak heights or peak areas are reported; where the latter are used, integrations of the signal were computer-generated automatically.

Nuclear magnetic resonance spectroscopy

The proton nuclear magnetic resonance (NMR) spectroscopy was performed on a Varian EM360L proton NMR spectrometer operating at 60 MHz. Probe temperature was 32°C. Solution concentrations were 9% solids. 3-(Trimethylsilyl)-1-propanesulfonic acid (2%), sodium salt hydrate (DSS) was added to samples as an internal standard. Chemical shifts of interest (ppm) were $=NC\underline{H}_2OH$ (4.80), DMDHEU ring protons (4.87), DHEU ring protons (5.00) and DHEU ring protons in the presence of $=NCH_2OR$ (5.6)[8].

The ^{13}C NMR spectroscopy was performed at the Lawrence Berkeley Laboratory, University of California, Berkeley, on a University of California Berkeley 250 MHz ^{13}C NMR spectrometer. A Nicolet 1180 computer interface and pulse programmer were used. Deuterium oxide and *p*-dioxane were added as lock and as reference, respectively. Bilevel decoupling was employed. Approximately 1000 scans per sample were run.

RESULTS AND DISCUSSION

Distributions of methylol derivatives of urea

Because urea can be present as an impurity in commercial preparations of DMDHEU[10], it was of interest to detect the presence of urea and its methylolated derivatives by HPLC analysis. Kumlin and Simonson had published equilibrium distributions of methylolated ureas in solutions containing formaldehyde to urea ratios of 1.4–4.0[11] (the theoretical maximum substitution is 4). These distributions, listed in Table I, were obtained from proton NMR analyses.

As formaldehyde increases, the relative amount of monomethylolurea decreases, trimethylolurea increases, and tetramethylolurea apparently never forms. The symmetrical dimethylolurea is formed preferentially to the asymmetrical dimethylolurea.

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* Names of companies or commercial products are given solely for the purpose of providing specific information; their mention does not imply recommendation or endorsement by the U.S. Department of Agriculture over others not mentioned.

TABLE I

DISTRIBUTION OF METHYLOL COMPOUNDS IN FORMALDEHYDE–UREA VIA PROTON NMR

From ref. 11. MMU = monomethylolurea; DMU = dimethylolurea; TMU = trimethylolurea.

Formaldehyde: urea ratio	*Mole % compound*	*Relative molar amount*	*Compound*
1.4	16.5	1	Urea
	44.0	2.7	MMU
	28.2	1.7	N,N′-DMU
	7.2	0.4	N,N-DMU
2.5	3.8	–	Urea
	25.6	1	MMU
	38.9	1.5	N,N′-DMU
	11.3	0.4	N,N-DMU
	0.5	0.5	TMU
4.0	0.2	–	Urea
	8.3	1	MMU
	38.5	4.6	N,N′-DMU
	6.6	0.8	N,N-DMU
	47.8	5.7	TMU

TABLE II

DISTRIBUTION OF METHYLOL COMPOUNDS IN FORMALDEHYDE–UREA VIA HPLC

Formaldehyde: urea ratio	*Retention time (min)*	*Relative peak heights*	*Peak assignments*
–	6.4	–	Urea
1	6.35	1	Urea
	6.95	2	MMU
	7.63	2	N,N′-DMU
2	6.37	1	Urea
	6.87	6	MMU
	7.63	20	N,N′-DMU
	8.13	3.5	TMU
3	6.50	1	MMU
	7.05	0.25	N,N-DMU
	7.625	1.5	N,N′-DMU
	8.375	3.7	TMU
4	6.55	1	MMU
	7.00	0.13	N,N-DMU
	7.65	1.72	N,N′-DMU
	8.35	1.08	TMU

TABLE III

DISTRIBUTION OF METHYLOL COMPOUNDS IN DMDHEU VIA PROTON NMR

Formaldehyde: DHEU ratio	*Relative peak heights*	*Protons from:**
1	1	DHEU
	0.625	MMDHEU
	0.75	DMDHEU
2	1	DHEU
	1	MMDHEU
	0.75	DMDHEU
3	1	DHEU
	1.1	MMDHEU
	1.4	DMDHEU

* MMDHEU = monomethyloldihydroxyethyleneurea.

Using the NMR data as a guide in assigning retention times, we employed reversed-phase HPLC to establish equilibrium distributions of methylolated ureas. The relative distributions, listed in Table II, parallel those from the published NMR data. As the formaldehyde to urea ratio increased, the amount of monomethylolurea relative to the di- and trimethylolated ureas decreased. No tetramethylolurea was detected. There was preference in methylolation to produce symmetrical dimethylolurea in considerably greater amounts than unsymmetrical dimethylolurea.

Distribution of methylol derivatives of 4,5-dihydroxyethyleneurea

Table III lists the relative peak heights in spectra obtained from proton NMR analyses of reaction solutions of formaldehyde and isolated DHEU. The formaldehyde to DHEU ratios were varied from 1 to 3 (theoretical maximum substitution is 2) under reaction conditions optimum for methylolation, 2 h at pH 5.5–5.9 and 80°C. Because the peaks are singlets for the protons of interest, even a 1:1:1 equimolar

TABLE IV

DISTRIBUTION OF METHYLOL COMPOUNDS IN DMDHEU VIA HPLC

Formaldehyde: DHEU ratio	*Retention time (min)*	*Relative peak heights*	*Peak assignments*
–	6.2	–	DHEU
1	6.25	1	DHEU
	6.75	5.17	MMDHEU
	7.40	6.68	DMDHEU
2	6.85	1	MMDHEU
	7.40	6	DMDHEU
3	6.85	1	MMDHEU
	7.30	4	DMDHEU

mixture of DHEU:MMDHEU:DMDHEU should give relative peak heights for DHEU ring protons to DHEU ring protons in the presence of $=NCH_2OR$ to methylene (methylol) protons of 1:1:2. Only in the solution containing 3 moles of formaldehyde per mole of DHEU are these ratios approached.

When these same reaction solutions were examined by reversed-phase HPLC analyses, conclusions regarding the quantitative distribution of methylol derivatives of DHEU were different (Table IV). Even at a formaldehyde to DHEU ratio of 1, MMDHEU and DMDHEU have increased markedly relative to DHEU. At a formaldehyde to DHEU ratio of 2, DHEU has disappeared, and the dimethylol derivative predominates. These peak height ratios are those expected from the low formaldehyde release characteristics of cotton fabric finished for durable press with an agent produced from a reaction solution containing 2 moles of formaldehyde per mole of DHEU[8]. Formaldehyde released to the environment from a finished fabric is a good measure of efficient cross-linking; as efficiency decreases, formaldehyde increases.

Detection of added urea in solutions of methylolated dihydroxyethyleneurea

From retention times established for urea and its methylol derivatives (Table I), an attempt was made to discern the lowest concentration of urea present in solutions of methylolated DHEU through HPLC analyses. Detection of low concentrations of urea in the presence of methylolated DHEU can assist in identification of the source of inefficient cross-linking from commercial DMDHEU solutions. These solutions are the unpurified reaction products of urea, glyoxal and formaldehyde rather than the products of isolated DHEU and 2 moles of formaldehyde. Incomplete reaction in a commercial product can result in the presence of free urea. Because methylolated ureas are inefficient cross-linkers, the presence of these agents to any extent in a commercial reactant can contribute to formaldehyde release[10]. Fig. 2 shows the lowest level of added urea detected in a solution of DMDHEU (from DHEU and 2 moles of formaldehyde) by HPLC analyses and by ^{13}C NMR analyses. Urea was added in concentrations from 1 mole percent based on DMDHEU to 25 mole percent based on DMDHEU. With ^{13}C NMR, the urea can be detected at the 1% level (emerging C=O peak of urea at 162 ppm next to the C=O peak of DMDHEU at 160 ppm). With HPLC the urea itself cannot be detected until the 10% level; however, the influence of urea on the DMDHEU:MMDHEU peak area ratios can be seen at lower levels. The percentage of DMDHEU steadily decreases from 90% with no added urea to 77% with 25% added urea.

Characterization of impurities in a DMDHEU solution

There are many possibilities for impurities in a DMDHEU solution prepared from urea, glyoxal and formaldehyde without isolation of a DHEU intermediate. Table V lists some of these impurities, together with retention times and peak assignments; these components reduce cross-linking efficiency. Where these impurities exist in equilibrium ratios of their reaction products with formaldehyde, addition of a pure compound for identification (spiking) is not feasible because introduction of the standards causes equilibrium shifts.

Comparisons of chromatograms of DMDHEU solutions

Fig. 3 shows chromatograms of a freshly prepared sample of DMDHEU from

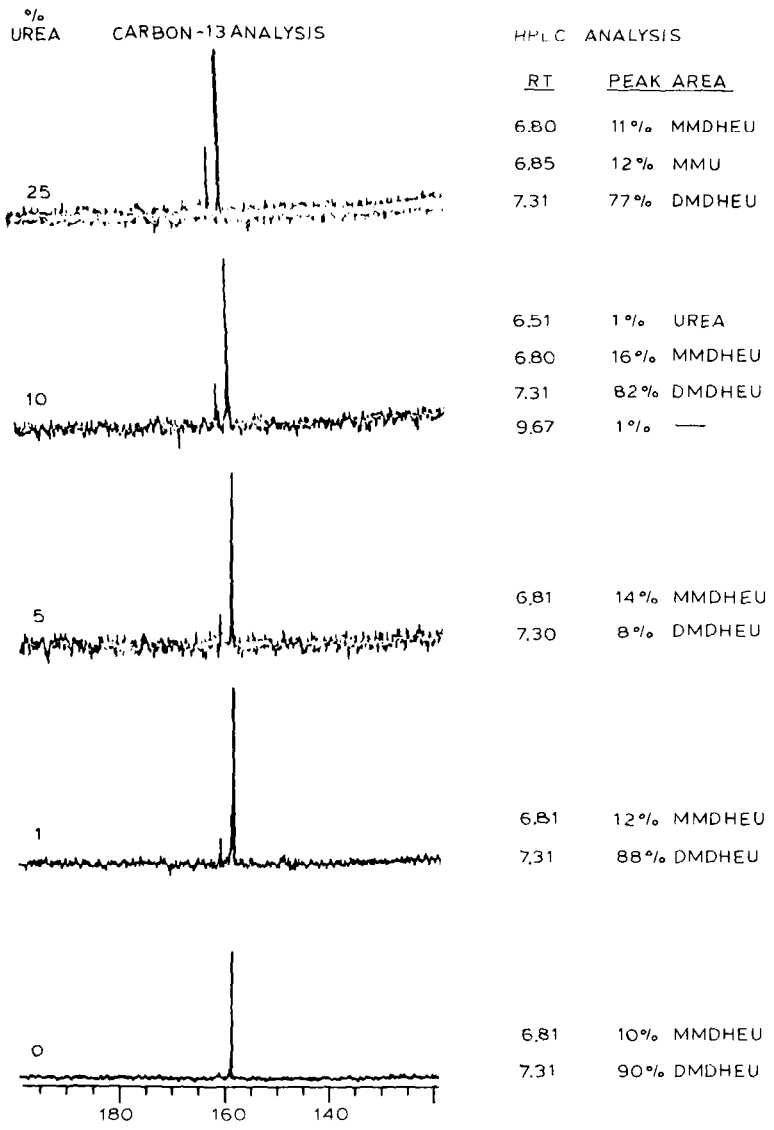

Fig. 2. Comparison of ^{13}C NMR analyses and HPLC analyses of methylolated DHEU solutions containing 0, 1, 5, 10 and 25 mole-% urea.

isolated DHEU and 2 moles of formaldehyde, and of a preparation from urea, glyoxal and 2 moles of formaldehyde (a commercial-type preparation). Differences between the two chromatograms are evident. The chromatogram from the commercial-type preparation shows a shoulder at 6.7 min, a peak for methylolated urea at 8.3 min and possibly a methylolated acetylenediurea peak close to 10 min. The single DMDHEU peak in the chromatogram from the isolated DHEU indicates that equilibrium among the methylolated derivatives of DHEU has not yet been established.

TABLE V

POTENTIAL IMPURITIES IN DMDHEU

DMA = dimethylolacetylenediurea; TMA = trimethylolacetylenediurea; TETRAMA = tetramethylolacetylenediurea.

Compound	*Retention time (min)*	*Relative peak heights*	*Peak assignments*
Glyoxal	6.0	–	
Glyoxylic acid	6.0	1	Glyoxal
	6.6	4	Glyoxylic acid
Glycolic acid	6.2		Glyoxal
	7.56		Glycolic acid
Oxalic acid	6.4	1	
	7.56	1.2	
Acetylenediurea–formaldehyde (1:2)	8.65	1	DMA
	10.8	1.4	TMA
	14.6	0.8	TETRAMA
Acetylenediurea–formaldehyde (1:3)	10.8	1	TMA
	14.5	1.6	TETRAMA
Hydantoin–formaldehyde (1:2)	10.9	1	
	14.3	1	
	14.5	2.1	
	19.1	0.85	
Urea	6.4	–	

Later chromatograms of the same solution show the resolution into the two peaks, DMDHEU and MMDHEU, seen in Table IV.

In Fig. 4 can be seen further effects of equilibrium changes in DMDHEU solutions, both with time and from addition of catalyst. Before overnight storage, this dilute DMDHEU solution had only two peaks. On inclusion of zinc nitrate

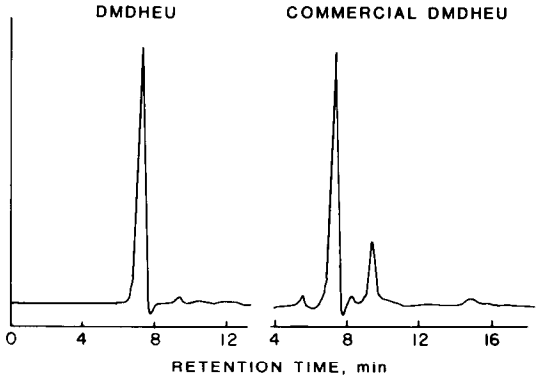

Fig. 3. Chromatograms of freshly prepared DMDHEU from DHEU–formaldehyde (1:2) and of commercial-type DMDHEU from urea–glyoxal–formaldehyde (1:1:2).

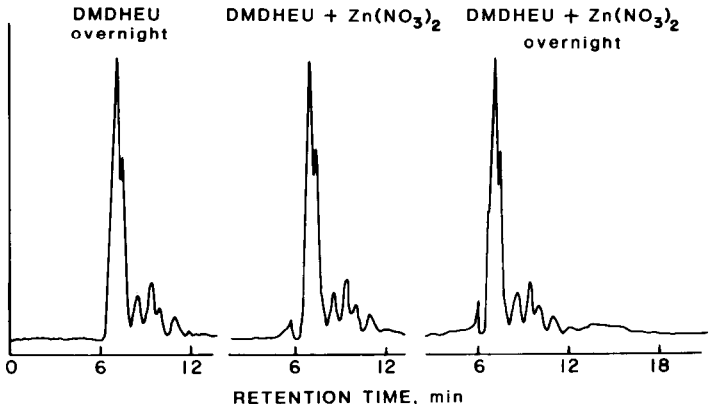

Fig. 4. Chromatograms of DMDHEU. (Left) allowed to stand overnight; (centre), with zinc nitrate added; (right) allowed to stand overnight with zinc nitrate added.

catalyst (retention time, 5.9 min) changes in the solution occur almost immediately; overnight storage does not further alter the solution composition.

Chromatography of etherified DMDHEU

An approach that the textile industry has taken to reduce formaldehyde release from finished textiles has been to etherify DMDHEU with methanol[12]. The maximum etherification of hydroxyl groups on DMDHEU produces a tetramethylated compound. In practice, only partial etherification is achieved. Fig. 5 shows chromatograms of a partially etherified DMDHEU and of a tetramethylolated DMDHEU, each allowed to stand overnight in the presence of zinc nitrate. As with the previous chromatography, water was the mobile phase. Immediately evident from the chromatogram of the tetramethylated DMDHEU is the failure of this compound to elute; even after 75 min, only zinc nitrate eluted. The chromatogram of partially methylated DMDHEU (from urea, glyoxal, formaldehyde and methanol) shows the equilibrium mixtures of methylolated DHEU as well as partially methylated products, methanol, and the impurities —methylolated urea, acetylenediurea and hydantoin.

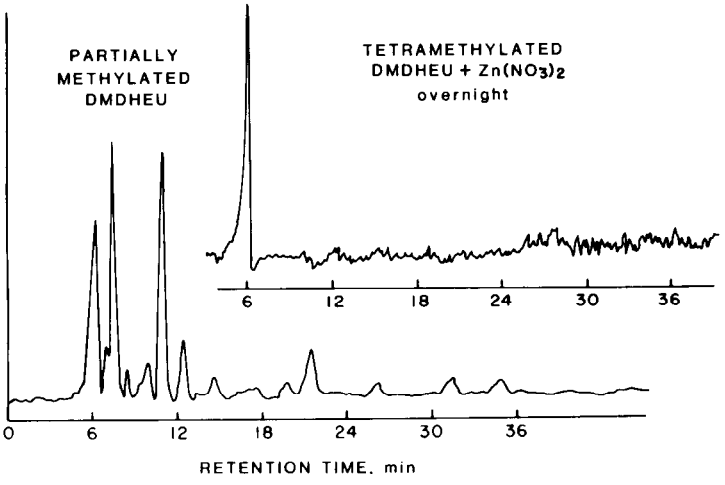

TABLE VI

RETENTION TIMES OF LESS POLAR DMDHEU DERIVATIVES WITH WATER–METHANOL AS THE MOBILE PHASE

NE = not eluted; NR = not retained.

Compound	*Retention times (min)*			
	Water in mobile phase (%)			
	100	*90*	*80*	*70*
4,5-Dimethoxy-1,3-bis(methoxymethyl) ethyleneurea	NE	30.8	24.8	14.5
4,5-Dimethoxy-1-methyl(3-methoxymethyl) ethyleneurea	NE	30.1	20.2	12.9
4,5-Dimethoxyethyleneurea	19.9	11.2	8.7	7.5
DHEU	6.2	NR	NR	NR

Although the tetramethylated derivative of DMDHEU, 4,5-dimethoxy-1,3-bis-(methoxymethyl)ethyleneurea, did not elute with water as the mobile phase, the compound will elute if part of the water is replaced with a less polar solvent. In Table VI are retention times of some of the more hydrophobic derivatives of DHEU as increasing percentages of water in the mobile phase are replaced by methanol. With DHEU itself, which has a retention time of 6.2 min with water as the mobile phase, replacement of water with as little as 10% methanol causes elution at the void volume. The increase in retention times with decreasing polarity of DHEU derivatives points up the hazard of assuming that, because reaction products do not elute with water as the mobile phase, they do not exist. Most conclusions from chromatography to characterize reagents for cellulose have assumed that these reagents are necessarily very polar.

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