Study of the Effect of DATEM. 1. Influence of Fatty Acid Chain Length on Rheology and Baking

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To answer the question of which fatty acid residue is the most effective, diacetyltartaric esters of monoglycerides (DATEMs) with fatty acids of chain lengths 6:0−20:0 were synthesized. The activity of synthesized DATEMs and commercial DATEM products was studied by means of rheological methods and a microscale baking test with 10 g of flour. Variation of the acyl residue from 6:0 to 22:0 showed that stearic acid (18:0) had the best effect on the baking activity of DATEM (loaf volume increased by 62%). DATEMs containing unsaturated fatty acids (18:1, 18:2) or DATEMs produced from diacylglycerols instead of monoacylglycerols showed a slight increase of the loaf volumes. A slight effect of DATEM on the rheology of dough was observed. However, much greater was the effect on the gluten isolated from doughs prepared with DATEM. The resistance of gluten to extension was increased after the addition of increasing amounts of DATEM (0.1−0.5%). Within the series of DATEMs derived from the homologous series of monoacylglycerols the product based on glycerol monostearate (18:0) showed a maximum increase of the gluten resistance.

Keywords: *DATEM; synthesis; 1-monoacylglycerol; wheat; microscale methods; baking performance; gluten rheology*

INTRODUCTION

Mono- and diacylglycerols esterified with mono- and diacetyltartaric acid, abbreviated DATEM, are anionic oil-in-water emulsifiers that are used throughout the world as improvers for bread-making. Among the benefits found for this class of synthetic emulsifiers are improvement of bread texture (Mettler et al., 1992) and volume (Nybo Jensen and Vrang, 1971; Lorenz, 1983; Rogers and Hoseney, 1983; Mettler and Seibel, 1993; Adams et al., 1994) retardation of bread staling (Birnbaum, 1955; Kulp and Ponte, 1981), increase in dough tolerance (Mettler et al., 1991a), and better dough properties during proofing (Mettler et al., 1991b) and baking (Mettler et al., 1991c). The effect of DATEM depends on its composition and on the baking performance of the flour.

DATEM is produced by the reaction of mono- and diacetyltartaric acid anhydride with monoacylglycerols or mixtures of mono- and diacylglycerols. Mono- and diacetyltartaric acid anhydride is synthesized from tartaric acid and acetic acid anhydride, and mono- and diacylglycerols are obtained by glycerinolysis of edible fats and distillation (Adams and Schuster, 1985). This procedure indicates that DATEMs, which are commercially available, are very complex mixtures of compounds. The improver effect of the commercial product is well characterized; however, up to now no information is available about the influence of the acyl residue on the effect of DATEM. The monoacylglycerols used in the commercial production process are very heterogeneous with respect to the chain length and degree of unsaturation of the acyl residue, as they are prepared from edible fats.

Microscale rheological methods and a microscale baking test on the basis of 10 g of flour have been developed in our laboratory (Kieffer et al., 1981a,b, 1993). These authors showed that these methods correlate highly with the corresponding standard methods using 1 kg of flour (Kieffer et al., 1998). Because a much smaller amount of material is necessary for the microscale methods in comparison to the standard methods, the effect of individual components isolated from DATEM or products synthesized on a laboratory scale on dough rheology and baking can now be determined.

In the present paper a systematic study to determine the influence of fatty acid chain length on the improver effect of DATEM is presented. Therefore, monoacylglycerols based on fatty acids with different chain lengths were synthesized and the corresponding DATEMs were prepared. The effects of these products on dough rheology and baking results are reported here.

EXPERIMENTAL PROCEDURES

Wheat Kernels and Wheat Flour. Samples of the German wheat variety Kraka from the 1992 harvest (Petersen, A.S., Lundsgaard, Germany) were conditioned to 14% moisture content and milled into flour with a Quadrumat Junior (Brabender, Duisburg, Germany). The flour was sieved (∅ = 0.2 mm) and allowed to rest for 2 weeks prior to use. The moisture content of the flour and kernels was determined according to ICC Standard 110 (1978b). The ash content was determined according to ICC Standard 104 (1978a). Nitrogen contents were determined by using the method of Dumas on a Leco FP328 nitrogen analyzer (Kirchheim, Germany). A conversion factor of 5.7 was used to calculate the protein content from the nitrogen content. Analytical characteristics of the flour were 14% moisture, 0.475% ash (dry mass), and 10.5% protein (dry mass).

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Chemicals. Acetic acid anhydride, 2,2′-dimethyl-4-(hydroxymethyl)-1,3-dioxolane (solketal), 4-(dimethylamino)pyridine (DMAP), [^{2}H]chloroform, and fatty acids 6:0, 8:0, 10:0, 12:0, 14:0, 16:0, 18:0, 20:0, 22:0, oleic acid (18:1), and linoleic acid (18:2) were obtained from Aldrich (Steinheim, Germany). Dicaprin (di-10:0) and distearin (di-18:0) were obtained from Sigma (Deisenhofen, Germany). All other chemicals were from Merck (Darmstadt, Germany).

Commercial DATEM Samples. Eight DATEM samples were obtained from two producers of DATEM.

Synthesis of 1-Monoacylglycerols. *Acetoneketals of 1-Monoacylglycerols.* To a solution of fatty acid (15 mmol; 6:0−20:0, 18:1, and 18:2), solketal (15 mmol), and DMAP (1.875 mmol) in diethyl ether (130 mL) at 20 °C was added dropwise a solution of *N*,*N*′-dicyclohexylcarbodiimide (DCC; 18.75 mmol) in diethyl ether (15 mL) to keep the temperature below 25 °C (Eibl et al., 1983). For docosanoic acid (22:0), carbon tetrachloride (300 mL) instead of diethyl ether was used as solvent. After 270 min of stirring at 20 °C, the suspension was filtered into a separation funnel and the filter was washed with solvent (25 mL). The solution was then washed twice with hydrochloric acid (HCl; 75 mL; 0.5 mol/L) and sodium carbonate solution (75 mL; 0.5 mol/L), respectively. Precipitated fatty acid was removed by filtration. The organic phase was then washed twice with sodium chloride (NaCl) solution (10% w/w; 150 mL) and dried over anhydrous sodium sulfate, and the solvent was removed by evaporation.

1-Monoacylglycerols. Acetoneketals of the 1-monoacylglycerols 10:0−22:0, 18:1, and 18:2 (4 mmol) were refluxed in methanol (25 mL)/HCl (2 mL; 1 mol/L) for 10 min. The solution was transferred into a separation funnel with diethyl ether/tetrahydrofuran (50 mL; 40:10, v/v), washed once with NaCl solution (50 mL; 10%, w/w), twice with sodium hydrogencarbonate solution (saturated at 22 °C; 25 mL), and twice with NaCl solution (50 mL; 10%, w/w). The organic phase was dried over anhydrous sodium sulfate, and the solvent was removed by evaporation. Acetoneketals of the 1-monoacylglycerols 6:0 and 8:0 (4 mmol) were hydrolyzed according to the method of Baer and Fischer (1945) in 10% (v/v) acetic acid (6:0, 300 mL; 8:0, 1000 mL) at 60 °C under stirring (6:0, 2 h; 8:0, 4 h). The resulting solution was extracted five times with diethyl ether (30 mL) and then treated as described above. The crude 1-monoacylglycerols were dissolved in diisopropyl ether (100 mL) and purified by column chromatography (20 × 3 cm i.d.) on silica gel G60 (50 g; 1.5% water). The column was flushed with diisopropyl ether and stepwise eluted with the following diisopropyl ether/acetonitrile mixtures (v/v): 100 mL 9:1, 50 mL each 8:2, 7:3, 6:4, 5:5, and 4:6. 1-Monoacylglycerols were eluted in fractions 4−6.

Synthesis of DATEM. A modified method according to Jacobsberg et al. (1976) was used.

Diacetyltartaric Acid Anhydride. Powdered tartaric acid (27 mmol), orthophosphoric acid (0.46 mmol), and acetic acid anhydride (90 mmol) were stirred for 25 min until the tartaric acid had dissolved. The mixture was then heated to 80 °C, a vacuum of 16 kPa (160 mbar) was applied, and the temperature was allowed to rise to a maximum of 110 °C while acetic acid (54.2 mmol, 3.1 mL) was distilled off.

DATEM. 1-Monoacylglycerols or diacylglycerols (1−2 mmol) were weighed into a pointed flask, and an aliquot of freshly prepared diacetyltartaric acid anhydride was added. The molar ratio 1-monoacylglycerol/diacetyltartaric acid was 1:0.95. The mixture was heated to 110 °C for 5 min or until it had been melted. The temperature was then increased to a maximum of 140 °C. At 139 °C a vacuum of 5 kPa was applied and acetic acid formed was distilled off for 3 min. The vacuum was removed, and the synthesized DATEM was allowed to cool.

Microscale Baking Test. This was performed as a micro rapid mix test (MRMT) with 10 g of flour according to the method of Kieffer et al. (1993) with some modifications. The ingredients based on the flour were as follows: NaCl, 2%; saccharose, 1%; yeast, 7%; ascorbic acid, 20 mg/kg. The final water content of the dough was 46.4%.

Preparation of DATEM Emulsions. In a 50 mL volumetric flask DATEM (500 mg) was heated for 3 min in a boiling water bath. Boiling distilled water (40 mL) was then added, and the mixture was immediately vortexed until a homogeneous emulsion had formed. The emulsion was cooled to room temperature by rinsing the flask with tap water and then made up to 50 mL with distilled water (1% w/v, stock solution). Aliquots of this stock solution (3.2, 6.4, 9.6, and 12.8 mL) were made up to 16 mL with distilled water. For baking (10 g of flour) 5 mL of the stock solution or the diluted solutions was used. In this way concentrations of 0.1, 0.2, 0.3, 0.4, and 0.5% DATEM based on flour were applied.

Dough Mixing. DATEM emulsion or water (5 mL, respectively) was cooled in the mixer to 15 °C for 1 min. Flour (10 g; 8.6 g of dry mass), a solution of NaCl and saccharose (1 mL; NaCl, 200 mg/mL; saccharose, 100 mg/mL), a solution of L-ascorbic acid (0.05 mL; 4 mg/mL), and yeast (0.7 g) were then added and mixed for 1 min at 1250 rpm. The final temperature of the dough was 26 °C.

Dough Handling and Baking. After removal of the dough from the mixer, it was allowed to rest for 20 min at 30 °C in a water-saturated atmosphere. The dough was then reshaped on a dough rounder for eight cycles. The resulting dough ball was passed through the rolls of a pasta machine to form an oval dough piece. This was rolled up and after a proofing time of 35 min at 30 °C in a water-saturated atmosphere, it was baked for 10 min at 230 °C. The oven (39 × 39 × 33 cm) was saturated with the vapor of 50 mL of water prior to baking. The volume of the bread was determined by measuring the amount of water displaced by the bread at room temperature. A vessel containing 500 mL of water was put on a balance, which was then adjusted to 0.0 g. The bread was impregnated with paraffin at 80 °C for 3 s, allowed to cool for 10 s, and then immersed in the water. The mass of the displaced water corresponded to the volume of the bread.

Microscale Rheology. Dough and gluten extensigrams were measured with the methods reported by Kieffer et al. (1981a,b) with some modifications. For dough rheology flour (10 g, 8.6 g of dry mass) and NaCl (0.2 g) were mixed in a microfarinograph for 1 min at 60 rpm and 22 °C. DATEM emulsion (5 mL) and distilled water were added, and the dough was mixed until a maximum consistency of 550 Brabender units (BU) was reached. The dough was removed, shaped to an ellipsoid form, and pressed into Teflon forms to give strands of 53 × 4 × 4 mm. After 40 min of resting in a desiccator at 22 °C in a water-saturated atmosphere, the strands were measured with an Instron 1122 Micro-Extensograph (Instron, Bucks, U.K). The extensibility of gluten was determined by mixing flour (10 g, 8.6 g dry mass) with DATEM emulsion (5 mL) and distilled water for 2 min so that a final dough consistency of 520−580 BU was reached. The dough was then washed with distilled water (540 mL) in a glutomatic (Perten Instruments, Huddinge, Sweden). The residue (gluten) was centrifuged in a test tube (100 × 13 mm i.d.) for 5 min at 4000*g* and 22 °C, pressed into Teflon forms, and treated as described above.

Gas Chromatography/Mass Spectrometry (GC/MS). GC analyses were performed by means of a gas chromatograph Type 5300 (Fisons, Mainz, Germany) equipped with a CP-SIL 5CB capillary (10 m × 0.25 mm i.d., 0.12 μm film thickness, Chrompack, Frankfurt, Germany) equipped with an on-column injector. An aliquot (0.5 μL) of the sample in chloroform [0.001% 1-monoacylglycerol (w/v)] was injected on-column at 60 °C. After 1 min, the temperature was raised at 25 °C/min to 300 °C, which was held for 15 min. Helium at a flow rate of 1.5−2.5 mL/min was used as a carrier gas. An MAT95S mass spectrometer (Finnigan MAT, Bremen, Germany) was connected with the gas chromatograph. The transfer line was heated to 300 °C. Negatively charged ions were generated by chemical ionization with ammonia at 115 eV using a source temperature of 250 °C, and the scan ran from *m*/*z* 100 to *m*/*z* 500.

Mass Spectrometry. Solutions of 1-monoacylglycerols in chloroform (0.05% w/v) were directly applied to the mass spectrometer (MAT95S) running in the chemical ionization mode with isobutane as the reagent gas, generating positively charged ions.

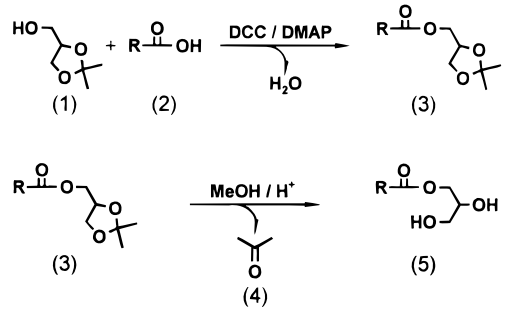

Figure 1. Synthesis of 1-monoacylglycerols: (**1**) 2,2-dimethyl-4-(hydroxymethyl)-1,3-dioxolane (solketal); (**2**) fatty acid; (**3**) acetoneketal of 1-monoacylglycerol; (**4**) acetone; (**5**) 1-monoacylglycerol; DCC *N*,*N*′-dicyclohexylcarbodiimide; DMAP, 4-(dimethylamino)pyridine; MeOH, methanol.

NMR Spectroscopy. ^{1}H NMR spectra were recorded in [^{2}H]chloroform by means of an AM 360 (Bruker, Karlsruhe, Germany). The ^{1}H signals were assigned according to tetramethylsilane (TMS) as the internal standard.

Other Analytical Procedures. Thin-layer chromatography was performed on HPTLC silica gel 60 plates (200 × 100 × 0.25 mm) according to the method of Dieffenbacher and Bracco (1978). Petroleum ether/diethyl ether/acetic acid (60:40:1, v/v/v) was used as eluent, the sample concentration was 4% (w/v) in dichloromethane/methanol (2:1, v/v) and the sample volume was 10 μL. Developed plates were air-dried and sprayed with 0.2% dichlorofluoresceine (w/v) in ethanol, and the spots were detected under an UV lamp (254 nm). Acid values of DATEM were determined by dissolving the sample (100 mg) in neutralized solvent (10 mL; diethyl ether/ethanol 50:50, v/v) and were titrated with ethanolic potassium hydroxide (KOH; 0.1 mol/L) until a pale red color appeared. Phenolphthalein [3 drops of a 1% (w/v) solution in ethanol] was used as an indicator. The acid value was calculated as milligrams of KOH per gram of sample. For the determination of the saponification value, 1-monoacylglycerol (100 mg) or DATEM (50 mg) was refluxed with ethanolic KOH (5 mL; 0.5 mol/L) for 60 min. The hot solution was mixed with phenolphthalein [3 drops of a 1% (w/v) solution in ethanol] and immediately titrated with HCl (0.5 mol/L) until the red color disappeared. The saponification value was calculated as milligrams of KOH per gram of sample.

RESULTS AND DISCUSSION

Wheat Flour. The flour used in this study (Kraka, 1992) had a poor bread-making performance due to its low protein content. This was also demonstrated by Kieffer et al. (1998), who found a loaf volume of only 35.5 mL for the same flour sample by means of the MRMT. Wheat varieties with good bread-making performance (i.e., Bussard, Monopol, Astron, DNS) produced bread volumes >60 mL. Despite this, the flour was used for the investigations because Adams et al. (1994) showed for the cultivar Kraka that the bread-making performance is substancially increased by the addition of DATEM.

Synthesis of 1-Monoacylglycerols. DATEM is synthesized by the reaction of monoacylglycerols and diacetyltartaric acid in the presence of acetic acid. To answer the question of which fatty acid residue is the most effective in DATEM, monoacylglycerols with fatty acids of different chain lengths had to be synthesized. The synthetic route used in this study is presented in Figure 1. Solketal (**1**) was acylated at the primary hydroxyl group by activation with DCC and DMAP as catalyst (Eibl et al., 1983; Neises and Steglich, 1985). A homologous series of aliphatic fatty acids (**2**) was used (6:0−22:0) including oleic (18:1) and linoleic acid (18:2) as unsaturated compounds. The intermediate ketal (**3**) was hydrolyzed with HCl in the presence of methanol or with 10% acetic acid (6:0 and 8:0; Baer and Fischer, 1945) to the corresponding 1-monoacylglycerol (**5**). The acylation proceeded with high yields (<68%; Table 1), whereas during hydrolysis of the intermediate (**3**) side reactions, that is, formation of fatty acid methyl ester or hydrolysis of the ester bond between ketal (**3**) and fatty acid, occurred. This was proven by thin-layer chromatography of the reaction products. To remove the free fatty acid and its methyl ester, the hydrolysate was purified by column chromatography on silica gel. Increasing amounts of acetonitrile in diisopropyl ether [10−60% (v/v)] were used as eluent. 1-Monoacylglycerols were eluted in fractions 4−6 in 18−51% yield as shown in Table 1.

Table 1. Yields (Percent) of the Synthesis of 1-Monoacylglycerols

	fatty acid										
compd	6:0	8:0	10:0	12:0	14:0	16:0	18:0	18:1	18:2	20:0	22:0
AK[a]	109	104	111	92	88	95	84	75	95	68	103
1-MG[b]	18	28	42	42	23	40	28	37	51	22	27

[a] Acetoneketal of 1-monoacylglycerol. [b] 1-Monoacylglycerol.

Table 2. Saponification Values (Milligrams of KOH per Gram of Sample), Melting Points (mp, °C), and Molecular Masses of Synthesized 1-Monoacylglycerols

	saponification value			molecular
1-MG	calcd	found	mp	mass[a]
6:0	295	281		190
8:0	257	257	34	218
10:0	228	218	49−50	246
12:0	205	208	58−59	274
14:0	186	200	62	302
16:0	170	172	71	330
18:0	156	149	75	358
18:1	157	154	28	356
18:2	158	151		354
20:0	145	144	77	386
22:0	135	140	79	

[a] Determined by mass spectrometry (direct inlet).

Characterization of 1-Monoacylglycerols. This was performend by the determination of the saponification values and the melting points and by the determination of the molecular masses by GC/MS or MS and by ^{1}H NMR measurements. Some of the results are reported in Table 2. The saponification values found for the 1-monoacylglycerols were in good agreement with the calculated ones. The melting points increased with increasing chain length of the fatty acid. Unsaturated fatty acids caused a decrease in the melting points of the monoacylglycerols. To check the purity of the monoacylglycerols, they were separated by GC and detected by MS. Negatively charged ions were generated by chemical ionization with ammonia. However, the molecular weights could not be directly determined by GC/MS. In all cases except fatty acids 6:0 and 8:0 the major signals (100%) were represented by the respective fatty acids; less intensity (<25%) was found for the ions generated by the elimination of water $(M - H_2O - H)^-$. Direct inlet of the monoacylglycerols into the MS system and generation of positively charged iones by chemical ionization with isobutane delivered the molecular masses of all monoacylglycerols except 22:0 (Table 2). The identity of glycerol monobehenate (22:0) was already proven by GC/MS as described above.

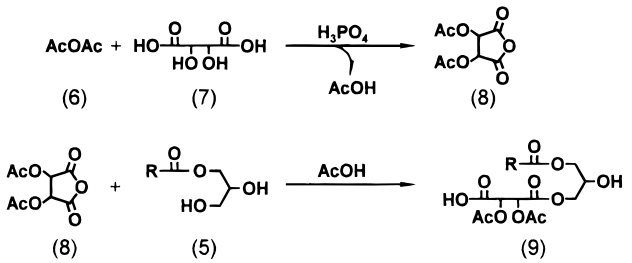

Figure 2. Synthesis of diacetyltartaric acid anhydride and DATEM: (**5**) 1-monoacylglycerol; (**6**) acetic acid anhydride; (**7**) tartaric acid; (**8**) diacetyltartaric acid anhydride; (**9**) diacetyltartaric ester of monoglyceride (DATEM).

^{1}H NMR studies of synthesized glycerol monocapronate and monopalmitate were performed to detect isomerization of the 1-isomer to the 2-isomer. 1- and 2-monopalmitate were used as standards. Differences in the spectra were detected between 3.5 and 5 ppm (spectra not shown). The spectra of the synthesized monoacylglycerols showed signals from both isomers. Quantification of the degree of isomerization gave 6.0 and 6.7% 2-isomer in the synthesized 1-glycerol monocapronate and 1-glycerol monopalmitate, respectively. This may be due to acyl migration during acid hydrolysis of the acetoneketals (**3**) or during column chromatography on silica gel (Serdarevich and Carroll, 1966; Serdarevich, 1967).

Synthesis of DATEM. Diacetyltartaric acid anhydride (**8**) was prepared according to the method of Jacobsberg et al. (1976) by dissolving tartaric acid (**7**) in acetic acid anhydride (**6**) and heating to 80 °C in the presence of catalytic amounts of phosphoric acid (Figure 2). The equilibrium of the reaction was moved to the formation of diacetyltartaric acid anhydride by removing acetic acid by distillation under reduced pressure while the temperature was increased to 110 °C. According to Jacobsberg et al. (1976) two-thirds of the theoretical amount of acetic acid was removed by distillation under reduced pressure. The rest of the acetic acid had a catalytic effect in the next step of the reaction and served as a solvent for diacetyltartaric acid anhydride. For the preparation of DATEM (**9**), diacetyltartaric acid anhydride (**8**) was reacted with the synthesized 1-monoacylglycerols (**5**) according to Figure 2 while the temperature was increased from 110 to 140 °C. The slight excess of monoacylglycerol that was used led to a complete conversion of diacetyltartaric acid. In addition to the 1-monoacylglycerols, two diacylglycerols containing capric (10:0) and stearic acid (18:0), respectively, were used for DATEM synthesis.

Characterization of DATEMs. This was performed by the determination of the acid values, the saponification values and, for solid samples, the melting points. These data are reported in Table 3. As expected, for the DATEMs based on the homologous series of monoacylglycerols the saponification values and the acid values decreased with increasing chain length of the fatty acid. Synthesized DATEMs were comparable to commercial products. This was demonstrated by a comparison of DATEM 18:0 with a commercial product containing 91% 18:0 (sample C of Table 4). Furthermore, the procedure of DATEM synthesis was reproducible. This was shown by the synthesis of a series of four DATEMs (18:0) under identical conditions (samples X1−X4). Within this series standard deviations for the acid values, saponification values, and melting points were 3.4, 3.7, and 2.9%, respectively.

Table 3. Characteristics of Synthesized DATEMs

DATEM	acid value (mg of KOH/g)	saponification value (mg of KOH/g)	mp (°C)
6:0	140	712	
8:0	143	629	
10:0	136	620	
12:0	126	580	
14:0	115	546	
16:0	120	530	30
18:0	107	510	47
18:1	109	516	
18:2	104	543	
20:0	101	490	55
22:0	94	396	63
di-10:0	114	522	
di-18:0	81	351	49
18:0 (91%)[a]	112	533	44

[a] Commercial product prepared by a producer of DATEM (sample C of Table 4).

Effect of DATEM on the Baking Performance. To determine the optimal amount of DATEM for baking, concentrations of 0.1−1% of DATEM with respect to the amount of flour were used for the baking tests. These experiments showed that concentrations exceeding 0.5% did not lead to a further increase of the loaf volumes. This observation was in accordance with the results of Adams et al. (1994), who found good baking performance at concentrations of 0.25 and 0.35%. Therefore, the following baking tests were performed with DATEM concentrations of 0.1−0.5%. With the commercial DATEM samples a maximum increase of the loaf volumes of 55−60% was observed. The optimal concentrations ranged from 0.3 to 0.5%. This is presented in Table 4. Within the series of four synthesized DATEMs X1−X4 on the basis of glycerol monostearate (see above), reproducibility of the whole procedure including the synthesis of DATEM and the microscale baking test was investigated. A concentration of 0.3% was used. For these samples an increase of the loaf volume of 46% was observed, showing that the synthesis produced DATEMs which were comparable with commercial samples. The standard deviation of the loaf volumes of ±4.5% showed the reproducibility of the synthesis and the baking test (Table 5). However, the increase of the loaf volume was not the only effect caused by DATEM. On addition of DATEM the surface of the doughs became less sticky and the doughs were much easier to handle. This observation is in accordance with results published by Mettler et al. (1991b,c, 1992).

DATEMs derived from the homologous series of monoglycerides were also applied in concentrations of 0.1−0.5%. Three baking tests were performed for each concentration. Furthermore, three control breads without DATEM were prepared for each synthetic DATEM. The maximal loaf volumes produced by the synthetic DATEMs are shown in Figure 3. The loaf volumes without addition of DATEM amounted to 34.0 mL with a standard deviation of ±6.1% (n = 51). Volumes increased with increasing chain length of the fatty acid present in DATEM (standard deviations of ±2.1−11.7%, n = 3, respectively). Most of the DATEMs showed optimal performance at concentrations of 0.2−0.4%. A maximum volume of 55 mL (standard deviation of ±4.4%, n = 3) was achieved with 0.2% of DATEM based on glycerol monostearate (18:0) corresponding to an increase of the bread volume of 62% (Figure 4). This result corresponds to baking tests performed with commercial DATEM samples shown in Table 4. DATEMs

Table 4. Microscale Baking Test with Commercial DATEM Samples: Bread Volumes (BV, mL) and Standard Deviations (SD, %)

concn[a] (%)	commercial DATEM sample							
	A, BV ± SD	B, BV ± SD	C, BV ± SD	D, BV ± SD	E, BV ± SD	F, BV ± SD	G, BV ± SD	H, BV ± SD
0[b]	34.0 ± 6.1	34.0 ± 6.1	34.0 ± 6.1	34.0 ± 6.1	34.0 ± 6.1	34.0 ± 6.1	34.0 ± 6.1	34.0 ± 6.1
0.1[c]	40.2 ± 8.3	47.4 ± 3.2	47.6 ± 2.2	50.1 ± 0.4	46.0 ± 3.2	46.6 ± 5.4	47.4 ± 2.5	46.7 ± 2.1
0.2[c]	48.6 ± 8.7	50.9 ± 2.5	50.7 ± 2.3	52.8 ± 0.3	53.5 ± 0.8	55.8 ± 2.7	47.2 ± 2.2	49.8 ± 0.4
0.3[c]	53.5 ± 1.3	53.7 ± 4.9	53.9 ± 1.3	53.6 ± 1.8	51.7 ± 0.7	52.5 ± 0.8	51.5 ± 1.3	47.9 ± 4.8
0.4[c]	47.7 ± 8.3	50.7 ± 1.7	51.6 ± 4.9	52.4 ± 2.9	49.8 ± 1.0	56.2 ± 3.3	52.8 ± 0.3	53.8 ± 3.1
0.5[c]	49.6 ± 4.3	50.3 ± 4.6	51.6 ± 1.0	52.2 ± 3.4	52.0 ± 1.9	52.9 ± 4.4	51.6 ± 3.5	53.3 ± 1.1

[a] Concentration based on flour. [b] BV and SD for $n = 39$. [c] BV and SD for $n = 3$.

Table 5. Microscale Baking Test with a Series of Synthetic DATEM Samples: Bread Volumes (BV, mL) and Standard Deviations (SD, %)

concn (%)	DATEM				total X1−X4, BV ± SD
	X1,[a] BV	X2,[a] BV	X2,[a] BV	X2,[a] BV	
0	34	33	35	34	34 ± 2.4
0.3	46	44	46	49	46 ± 4.5

[a] Synthetic DATEM sample (100% 18:0).

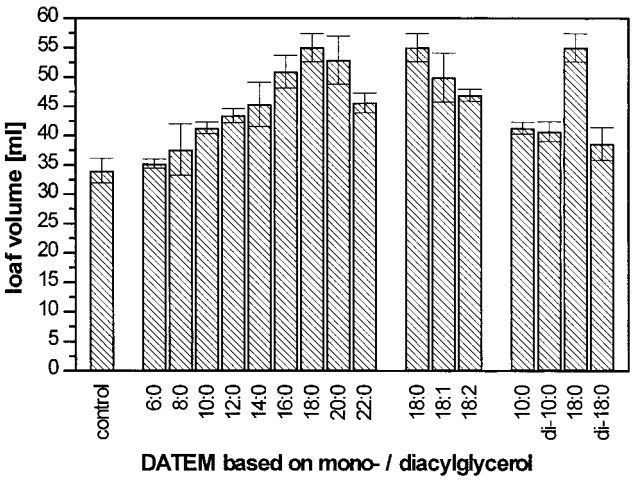

Figure 3. Microscale baking test with synthesized DATEM samples. Maximum loaf volumes were obtained by the addition of DATEM. Concentration = 0.1−0.5% of flour weight.

with fatty acids longer than 18:0 increased the loaf volumes, but they were not as effective as DATEM based on monostearate. Short-chain fatty acids (6:0, 8:0) in DATEM had a detrimental effect on the baking performance. For some concentrations even a decrease of the loaf volume was observed (up to −6%). For DATEM based on 6:0, bread flavor was not acceptable because of the release of caproic acid during baking. DATEMs on the basis of diacylglycerols improved the bread volume, but they were not as effective as the corresponding DATEMs on the basis of monoacylglycerols. This is especially true for the DATEMs based on stearic acid (18:0 loaf volume, +62%; di-18:0 loaf volume, +13.5%). DATEMs containing unsaturated fatty acids (18:1, 18:2) were not as active as the corresponding DATEM based on glycerol monostearate. In this series DATEM containing linoleic acid (loaf volume, +37.9%) was less effective than DATEM containing oleic acid (loaf volume, +46.8%).

Effect of DATEM on Dough and Gluten Rheology. The effect of DATEM during dough mixing in the farinograph was demonstrated by using the synthetic DATEM 18:0. The results are shown in Figure 5. Dough development time (time to peak) was strongly delayed by the addition of DATEM from 1.5 min in the dough without DATEM to 6 min in the dough containing 0.5% DATEM. However, the stability of the dough prepared with DATEM was small (1 min); the maximum peak was more pronounced, as in the control dough where the consistency remained the same for 3.5 min. The dough consistency after 15 min was higher when DATEM had been added (510 BU instead of 490 BU).

Dough rheology was tested by extensograph measurements after addition of synthesized DATEMs. However, only a slight effect of DATEM on dough rheology was observed. This is in contrast to results of Stampfli et al. (1996), who observed the dough strengthening effect of DATEM after addition of 1−2% of additive in contrast to 0.1−0.5% in the present study. For gluten rheology the mixing of dough and the isolation of gluten had to be modified to determine a DATEM effect. In the first attempts dough was prepared in the presence of NaCl and was washed with 2% NaCl solution. However, in the gluten prepared in this way, no effect of DATEM could be observed. Obviously, the NaCl present during mixing and washing of the dough extracted the DATEM from the gluten. Another explanation for the detrimental effect of NaCl is the fact that NaCl itself acts as a dough strengthener and competes with DATEM. If chloride ions are bound to positively charged gluten proteins, the net charge of the gluten is reduced and the interaction of the anionic emulsifier DATEM with gluten is reduced or even inhibited. A rheological effect of DATEM could be observed as soon as NaCl was omitted during dough mixing and washing. The mixing time was reduced to 2 min, because longer mixing times, even to the maximum of the farinogram curve, did not lead to a further increase of the effect. The synthesized DATEMs 6:0−22:0 were added in concentrations of 0.1−0.5%. As an example, the gluten extensigrams obtained after addition of DATEM based on glycerol monostearate (18:0) are shown in Figure 6a. The rheological effect

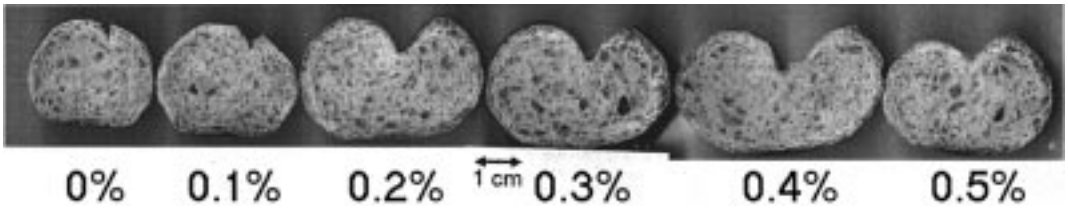

Figure 4. Minibreads obtained without (0%) and with 0.1−0.5% DATEM based on glycerol monostearate (18:0).

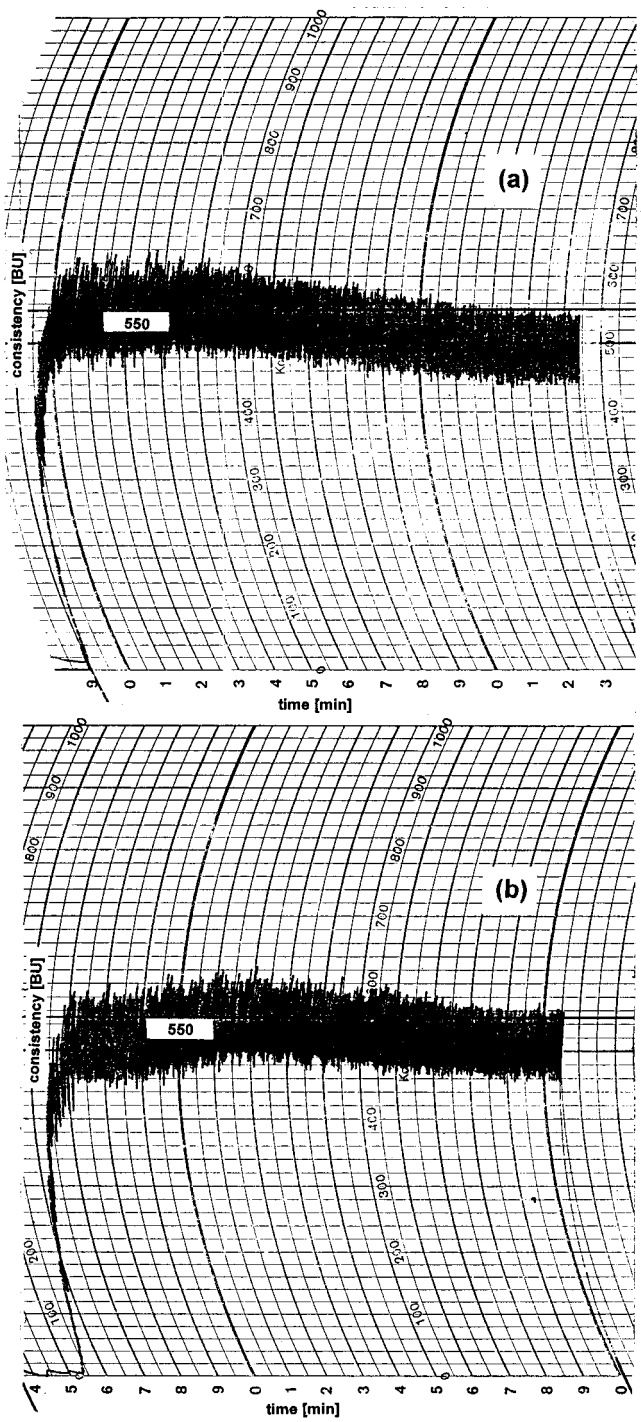

Figure 5. Mixing behavior of Kraka flour (a) without and (b) with 0.5% DATEM based on glycerol monostatearate. Conditions: mixing temperature, 22 °C; 2% NaCl; water absorption, (a) 5.56 mL and (b) 5.60 mL.

of DATEM on gluten is clearly dependent on the concentration of DATEM. An increase of the DATEM concentration led to an increase of the resistance and to a decrease of the extensibility of guten. An optimal concentration of 0.2−0.4% as for the baking tests was not present for gluten rheology. A comparison of the rheological effect of different DATEMs (6:0, 18:0, and 22:0) is shown in Figure 6b. A tendency for the increase of the gluten resistance and the decrease of the gluten extensibility after the addition of DATEM (0.5%) is present in all samples but to a different extent. Maximal resistance to extension (increase of 96%) was produced

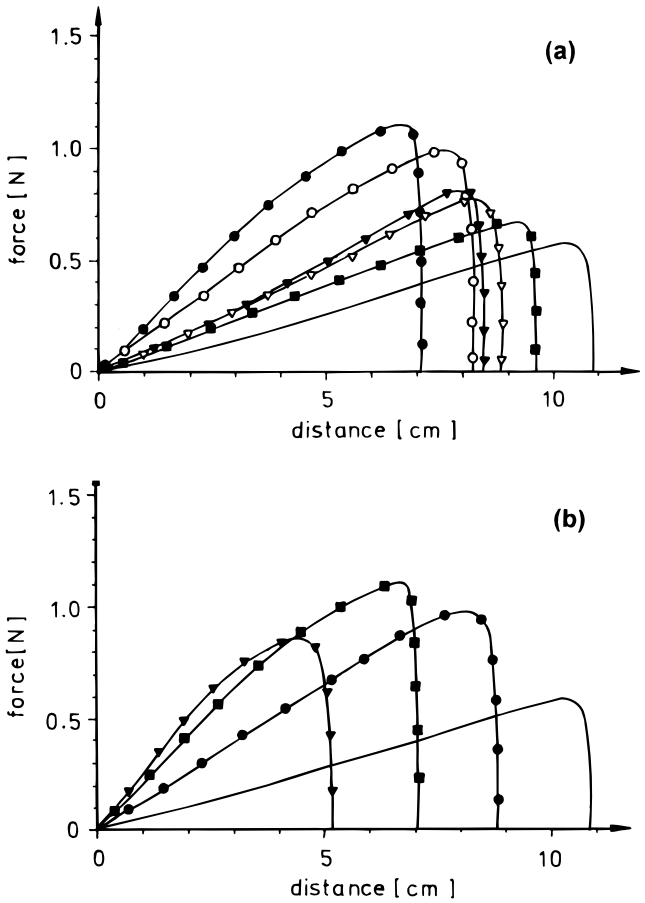

Figure 6. Microextension tests with gluten isolated from doughs prepared with **(**a**)** DATEM on the basis of glycerol monostearate (18:0) [(—) control; (■) 0.1%; (▽) 0.2%; (▼) 0.3%; (○) 0.4%; and (●) 0.5% DATEM] and **(b)** DATEM (0.5%) based on (▼) glycerol monocapronate (6:0), (■) glycerol monostearate (18:0), and (●) glycerol monobehenate (22:0) [(—) control].

by DATEM based on glycerol monostearate (18:0). The second effect of the DATEMs was a decrease of the extensibilty. This parameter was minimal for DATEM containing caproic acid (6:0; −52%) and maximal for DATEM containing behenic acid (22:0; −19%). From these results it can be assumed that the effect of DATEM on the gluten resistance may be correlated with its effect on the baking performance, because DATEM on the basis of 18:0 showed the best baking performance and produced the highest increase of the gluten resistance.

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