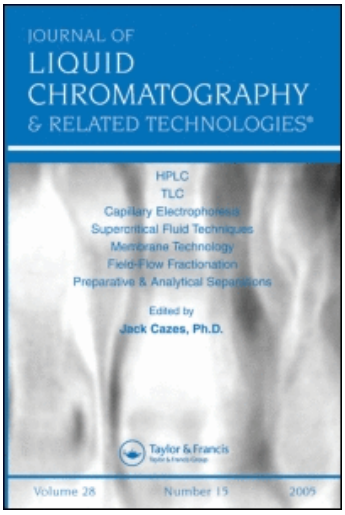

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MIXED-MODE GPC USED TO CONTROL THE REACTION BETWEEN *N,N*-DIMETHYL-PROPYLENE-1,3-DIAMINE AND TRIGLYCERIDES

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ABSTRACT

Gel permeation chromatography (GPC) was utilised to control the progress of the reaction between *N,N*-dimethylpropylene-1,3-diamine (DMPDA) and triglycerides (fats). As per "ideal size exclusion mode", the sample is separated into triglycerides (TGC), diglycerides (DGC), monoglycerides (MGC), and glycerine (GC), as the component groups with sufficiently different molecular weights. Moreover, the separation was obtained for MGC and amidoamines (AA), i.e. the reaction products, despite the fact that their molecular weights are the same in practice (Mw=348 and 358, respectively). The increased retention time for amidoamines was assumed to be accounted for by the additional adsorption effects in "adsorption mode". Resulting from the overlapping of two types of chromatographic separation mechanisms, an analytical method was obtained which could be called "mixed mode" conditions.

This method allows for the control of the amidolysis reaction of fats at its intermediate stages. The method is applicable for the respectively narrow distribution of molecular weights of triglycerides, which is the case in lard, sunflower oil and/or rape-seed oil.

INTRODUCTION

Alkylamidoamines, the derivatives of *N,N*-dimethylpropylene-1,3-diamines, make the second biggest produced group – after tertiary fatty alkyldimethylamines – of basic raw materials for the synthesis of cationic surfactants. They are applicable in the production of auxiliaries for various industries as well as improving agents for make-ups and household chemical formulations (quaternary ammonium salts, amine oxides, betaines etc.).[1] They also are alternative feedstocks for said fatty alkyldimethylamines which are produced in energy-consuming pressurised processes from fatty alcohols or primary fatty amines.

Alkylamidoamines can be produced by aminolysis (amidation) of fatty acids, fatty acid chlorides, fatty acid methyl esters (FAME), or by direct reaction of fats with polyamines (e.g. *N,N*-dimethylpropylene-1,3-diamine).[2] The fats (triglycerides) were selected as the basic feedstock since the ester system in FAME and in fats is advantageous from the energy point of view (considerably lower energy of the C-O bond at the carbonyl group than that in acids, and hence the possibility of conducting the synthesis at much milder conditions) and the hydrolysis or transesterification (to acids or FAME) stages could be omitted.

The synthesis of amidoamines directly from fats follows the presented scheme (Figure 1) of subsequent-parallel reactions which yield diglycerides (DGC) and monoglycerides (MGC) as intermediates as well as glycerine (GC) by-products. The analytical control of the reaction, inclusive of its intermediate steps, provides some essential contribution to the synthesis process and definition of the influence of process parameters on the reaction yield.

The titrimetric methods (determination of cationic surfactants) and potentiometric methods (determination of the contents for individual amine types: primary, secondary, and tertiary) are used for the analysis of cationic surfactants (fatty amines, amidoamines, and their quaternary derivatives) in mixtures.[3]

The specific and selective information on the composition of amidoamines can be obtained with the use of the chromatographic procedures, and in particular the liquid chromatography (HPLC) or thin-layer chromatography (TLC) methods.[4,5,6] On the other hand, the GPC method is known for its applicability in the analysis of polymers and/or fat oxidation products.[7,8]

Any chromatographic process covers the selective separation of the components being analysed between the stationary and mobile phases. In the case of gel permeation chromatography (GPC) operated in the size exclusion mode, the separation results from the differences in the hydrodynamic size of the molecules. The stationary phase is a porous gel with the defined pore size.

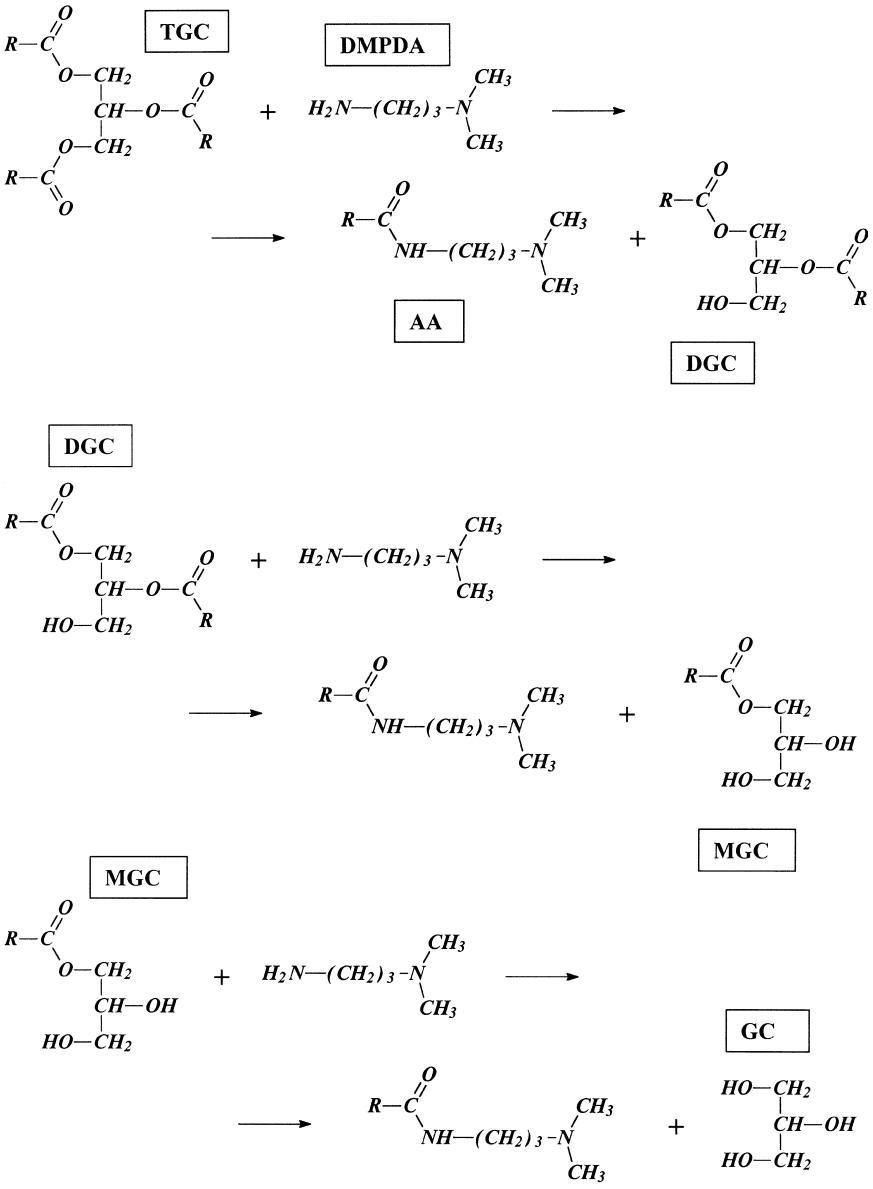

Figure 1. Aminolysis scheme for triglycerides.

Depending on the molecular size, a higher or lower number of pores is available for the specific molecule fraction. The smaller the molecules are, they can penetrate into the higher number of pores and, thus, they can stay longer in the stationary phase. Hence, the bigger molecules undergo elution first and then the smaller ones follow.

The above definition refers to the "ideal SEC" condition, i.e. completely no adsorption, electrostatic, or other interactions between the molecules of the components analysed and the stationary phase. Under real conditions, one should expect some additional effects which change with the solvent type employed as a mobile phase.[9] The conditions are close to ideal when, for example, high molecular weight polymers are analysed, especially those containing no active functional groups. Hence, GPC is generally thought to be best applicable for finding molecular weights for the polymers above 500 or even 1,000 Daltons. The changes of the elution times (retention times) for the components which are not caused by the molecule size but which result from the chemical structure of molecules or the solvent type are generally known and frequently referred to .[10] This is clearly visible, in particular, in the case of lower molecular weights, where the molecule size effect is relatively less important for the retention time.[11]

The use of GPC for the analysis of lower molecular weight compounds is more and more attractive since within this range some small differences in molecular weights can give considerable differences in the properties of the oligomers studied. Thus, a series of stationary phases is offered with the low average pore size (50, 100 Å) which have been intended for the separation of molecules within the range of from 100 to 1,000 Daltons.

This study investigates the possibility of controlling the reaction between lard and DMPDA with the use of the separation of component groups as per their molecular weights. Within the low molecular weights, the GPC method was assumed to make it possible to separate the unreacted triglycerides (Mw = 860), diglycerides (Mw = 604), and monoglycerides (Mw = 348), which are intermediates, and glycerine (Mw = 92). These components have sufficiently different molecular weights. The principal reaction product, amidoamine with the molecular weight of Mw = 358, should be eluted (under 'ideal SEC' conditions) together with monoglycerides.

EXPERIMENTAL

Reagents and Materials

N,N-dimethylpropylene-1,3-diamine - 99 % (from BASF, Germany). Technical grade lard (animal fat, melted, hard, as per Branch Standard BN-89/8186-01), with the following parameters:

Fat content	99.8 %
Acid number	0.41
Saponification No.	194.23
Glycerine	analytically pure, from POCH Gliwice, Poland.

Samples for tests were collected from the direct lard aminolysis process with various volumes of DMPDA.

The chromatographic investigations were carried out in a stand comprising: pump L-7100 from Merck-Hitachi, metering valve Knauer with the volume dosed of 20 μL, refractometer detector HP1047A from Hewlett-Packard, and de-gassing unit from Knauer. The detector signals were collected and processed by the software 'GRAMS/386 for Chromatography' (Galactics, USA). The separation took place in a set of three columns (in series): Plgel MiniMIX E and Plgel MiniMIX C (Polymer Laboratories) with the diameter of 4.6 mm and length of 250 mm, and Styragel HR4E (Waters, USA) with the internal diameter of 4.6 mm and length of 300 mm. Tetrahydrofuran (THF) with the purity of '*for HPLC'* from Merck (Germany) was used as the eluent. Its flow was 0.3 mL/min. The sample (about 100 mg) was dissolved in 10 mL THF.

RESULTS AND DISCUSSION

Under the GPC analysis conditions adopted, amidoamines were found to be eluted after monoglicerides despite their higher molecular weight (358 and 348 for monoglycerides). Thus, a satisfactory separation was obtained for these two groups of components (Figure 2) even when there was a few percent of monoglycerides and over 90 % of amidoamines in a sample. The individual component groups resulting from lard aminolysis were eluted at the following retention times: TGC = 27.9, DGC = 28.6, MGC = 29.6, AA = 30.3, and GC = 31.9 minutes.

The amine which was used in the reaction, DMPDA, at the concentration three times less than the sample concentration, does not appear in the basic part of the chromatogram. The comparison was presented in Figure 2 for the exemplary chromatograms for samples collected from the reaction mixtures with changing initial molar ratios of lard and DMPDA.

It was found in the optimisation of the method that the increased sample concentration improved the accuracy of the glycerine determination since the effect from the system (i.e. solvent signal beyond 32 minutes) was reduced. However, the separation of monoglycerides (MGC) and amidoamines was adversely affected. The opposite effect was observed for lowering the sample concentration, i.e. the accuracy of MGC determination is improved while that for glycerine is inferior. In order to be able to control the composition, the sample concentration of 100 mg/10 mL THF was adopted.

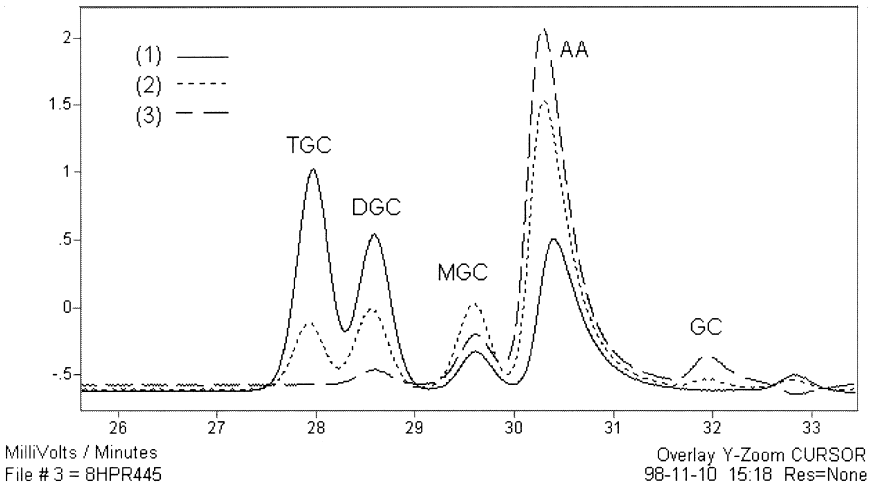

Figure 2. Comparison of chromatograms for samples collected from the reactions run at the amine-to-triglyceride molar ratios: (1) = 1:1, (2) = 2:1 and (3) = 3:1; TGC - triglycerides, DGC - diglycerides, MGD - monoglycerides, AA - amidoamines, GC - glycerine.

The increase of the eluent rate to 0,4 mL/min. gave no improvement of the separation performance of the system. Since the amine (DMPDA) employed in the reaction can not be seen in the chromatogram, its unreacted residue must be determined by other methods (potentiometric), yet it has no effect on the quantitative determination of the components discussed.

The analysis of the RI detector response revealed that for lard and amidoamines this is more or less the same, and its accuracy falls within 5 %. A lower detector signal was found for glycerine and the correction factor of f = 1.12 was determined; this was employed to adjust the peak area. The quantitative determinations were carried out with the use of the internal standardisation method. The average deviation for the determinations of TGC, DGC, MGC and AA was found to fall below 2 %. The average deviation for glycerine is higher and it reaches 6 %.

The analytical method presented demonstrates how misleading the determination of molecular weight can be for low molecular weights when the sample components reveal activity in relation to the column packing. In this case, the offset for the retention times can be expected to result from the presence of nitrogen atoms in the molecules.

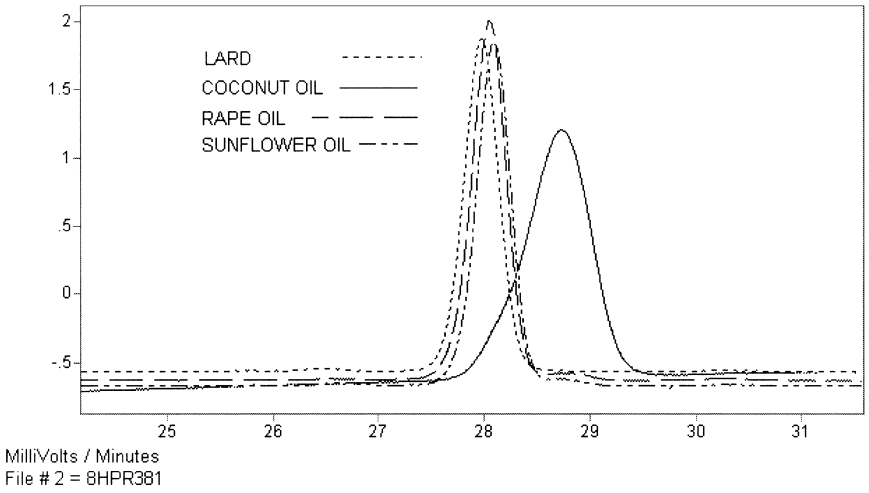

Figure 3. Comparison of GPC chromatograms for various types of triglycerides.

This seems to be confirmed by the observation, during the study, of complete absence of any signal for the initial amine where the nitrogen atoms take even higher share with the lower molecule size. In the analysis of the derivative of lard and diethylenetriamine (three nitrogen atoms), the peak of this monoamide (MW = 359) undergoes elution even further, i.e. after 32 minutes. This confirms a very strong effect from the basic functional groups on the retention time at the same molecular weight.

The additional effects (apart from SEC) which modify advantageously the retention time, made it possible to develop a useful method for the quantitative analysis of individual component groups. The peaks in a GPC chromatogram are much wider than those obtained from HPLC. Hence, the quantitative determination error found was thought to be normal and resulting principally from the difficulties in finding the proper integration ranges for individual peaks.

However, it should be remembered that another condition necessary for obtaining separation is the span of the distribution of TGC analysed, i.e. the distribution of DGC, MGC, and amidoamines. Figure 3 compares chromatograms of a few types of triglycerides. The molecular weights for triglycerides obtained from lard are much similar to those from sunflower oil and rape-seed oil, regarding both the molecular weight values and their distribution. Triglycerides from the coconut oil reveal the lower average molecular weight, but what is important is that the distribution is much wider.

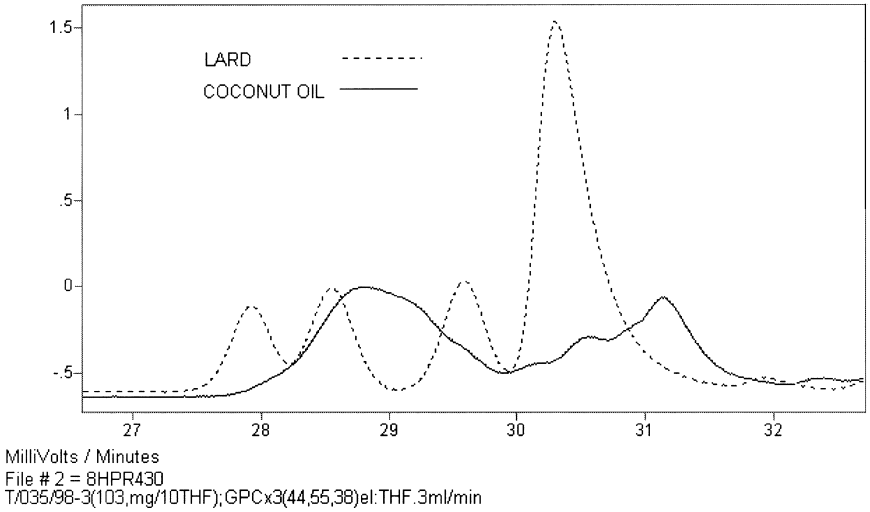

Figure 4. Comparison of chromatograms for mixed products obtained from the aminolysis of lard and coconut oil.

In Figure 4, the chromatograms were compared for the coconut oil and lard samples. Amidoamines, in this case, were shifted slightly over 31 minutes and some distortion of the glycerin peak can be observed. Resulting from the wide distribution of its molecular weights, the residual oil overlapped with diglycerides and monoglycerides in the region of 28 to 31 minutes. The chromatogram can not be subjected to such a selective interpretation as in the case of lard.

CONCLUSION

The additional effects which are disadvantageous in the molecular weight determinations by means of GPC made it possible to separate the amidoamine and monoglyceride groups despite their same average molecular weights (358 and 348, respectively). Hence, a simple, easy, and useful analytical method for group composition could be developed to be employed in kinetic investigations. It combines the separation of components with considerably different molecular weights (TGC, DGC, MGC + Amidoamines, Glycerine) in "size exclusion mode" with the separation of components with the same average molecular weights but with considerably different chemical structures (MGC and Amidoamines), probably in "adsorption mode." This justifies the use of 'mixed-mode' in the title of this paper.

It should, however, be remembered that the properly narrow distribution of molecular weights for triglycerides in the initial feedstock is a prerequisite for the method to be applicable, which has been satisfied in the case of lard.

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