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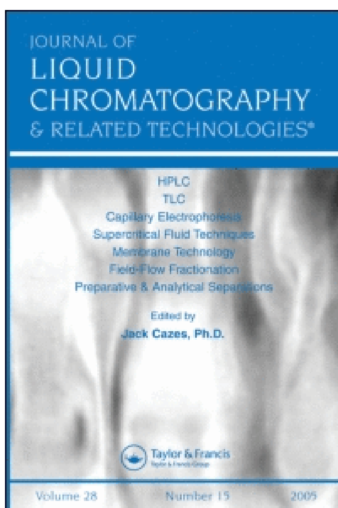

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REVERSED PHASE HPLC OF OXYETHYLATES OF *N*-METHYLANILINE AND *N*-ETHYLANILINE

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ABSTRACT

The conditions were selected for the reversed phase HPLC separation (phosphate buffer pH = 7.4 / methanol) of *N*-oxyethylates of *N*-methylaniline and *N*-ethylaniline on C18 columns, depending on the oxyethylene chain length. The use of the "mixed-mode" C18/anion column provided the possibility for simultaneous separation of oxyethylates, as well as, *N,N*-dimethylaniline and *N,N*-diethylaniline. UV spectra were taken for the compounds studied in order to find the optimum wavelengths for the detection procedure.

INTRODUCTION

The manufacturing process for methyl-, ethyl-, and butylethyleneglycols monoethers, – which are solvents in waterborne paints and/or brake fluids, – requires that the alcohol (i.e. methanol, ethanol, or butanol) is subjected to oxyethylation with oxirane (ethylene oxide). Alkaline catalysts like NaOH, KOH, or tertiary amines are used to make the reaction proceed at lower temperatures. Our earlier investigations revealed that the tertiary amine catalysts

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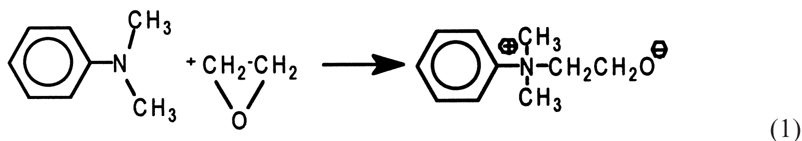
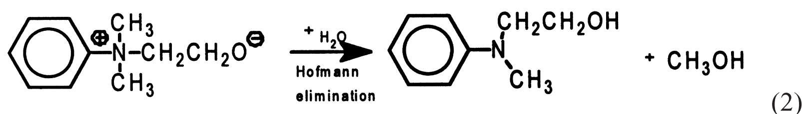
were also exposed to ethoxylation in the reaction mixture after their dealkylation.[1-3] The formed by-products are also amines and they keep on providing the catalytic activity for the basic process. In the case when *N,N*-dimethylaniline (DMA) is employed as a tertiary amine catalyst, the side reactions proceed as follows:

The oxirane molecule is added to the nitrogen atom at the first stage which yields a quaternary zwitterion; this becomes a precursor for the basic reaction, i.e. ethoxylation of alcohol.



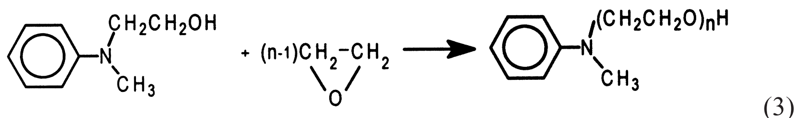
(1)

In the side-process, this ion is subjected to the Hofmann elimination where a methanol molecule [or ethylene molecule in the case of *N,N*-diethylaniline (DEA)] is removed and *N*-methyl-*N*-ethanolaniline (MA1EO) is formed.



(2)

The resulting product, with a satisfactorily active –OH group, reacts with further oxirane molecules as if it were a basic feedstock – alcohol. The homologous series of *N*-oxyethylated anilines (MAnEO) is yielded from this process.



(3)

The main products obtained from oxyethylation of low-molecular-weight alcohols can be analyzed, without any problem, by means of capillary gas chromatography.[4-8]

Many difficulties have to be overcome in direct GC analysis of *N*-ethylaniline ethoxylates.[9] Better results are obtained from GC separation and identification of ethoxylated 4-alkylanilines after anilines have been converted into trimethylsilyl derivatives.[10,11]

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The catalyst concentration in the reaction mixture considered is initially below 0.2% wt. After the catalyst is converted, the concentrations for individually formed by-products (MAnEO) drop down below 0.01 wt%. It is questionable to employ GC for quantitative investigations of such low concentrations of high-boiling amines in such a diversified matrix of regular products. Hence, the liquid chromatography (HPLC) method and sensitive UV detection was selected for the analysis of aniline catalysts, and that was presented in this paper.

EXPERIMENTAL

The following equipment was used to study the chromatographic separation: pump L-7100 from Merck-Hitachi (Darmstadt, Germany), degaser, injection valve (20 μL loop) and photometer from Knauer (Berlin, Germany). The detector data were collected and processed by means of software "Grams/386" from Galactics (Salem, MA, USA). The UV spectra were taken with the use of chromatograph HP1090 Hewlett Packard (Palo Alto, CA, USA) equipped with diode array detector.

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N,N-Dimethylaniline and *N,N*-diethylaniline were purchased from Avocado (Heysham, England), methanol and NaH_2PO_4 from POCH (Gliwice, Poland), and oxirane from Petrochemia (Plock, Poland). Methanol with the purity "for HPLC" was obtained from Merck (Darmstadt, Germany). Water, applicable in HPLC, was prepared by distillation and deionization and HP661 Water Purifier Hewlett Packard (Palo Alto, CA, USA) was employed for that purpose.

A phosphate buffer (prepared as the 0.01 M NaH_2PO_4 solution with 0.5 N KOH to adjust pH = 7.4) and methanol were used as the eluent components.

The ethoxylated alcohol samples were produced at Detergents Division of Institute of Heavy Organic Synthesis (Kędzierzyn-Koźle, Poland) in a 2 dm^3 stainless steel autoclave, equipped with the mechanical stirrer and pressure and temperature control systems. Alcohol, with the catalyst dissolved in it, was charged to the reactor and air was removed by means of compressed nitrogen; the temperature was increased to the reaction level and ethylene oxide was charged from a cylinder.

After preliminary screening tests, a phosphate buffer with pH = 7.4 was selected for the HPLC analysis and the following conditions were adopted: methanol gradient from 5 to 60% over 30 minutes and eluent flow rate of 0.6 mL/min. The samples to be analysed were dissolved in the phosphate buffer. The concentrations employed were 5 to 20%, depending on the catalyst concentration in the reaction.

RESULTS AND DISCUSSION

Satisfactory separation was obtained for successive homologues of oxyethylated anilines when the C18 column was operated under the conditions as above. There was, however, one disadvantage: the peak of unreacted aniline overlapped one essential peak representing a component with the oxyethylene chain. Figure 1 shows the chromatogram obtained from the column Purospher C18 80A, 125 x 3 mm, Merck (Darmstadt, Germany). The peaks for oxyethylates of *N*-methylaniline (MAnEO) are, in general, separated very well. However, a compound with six oxyethylene segments (MA6EO) is eluted together with initial *N,N*-dimethylaniline (DMA). The symbol of X stands for an unknown component which is present in the initial DMA.

The problem of overlapping peaks of initial amine and oxyethylated derivatives obtained, therefrom, was resolved by the use of the column "MIXED-MODE" C18/ANION, 300A, 150 x 4.6 mm, Alltech (Deerfield, USA). The results for the same sample were presented in Figure 2. That column has the C18 functional groups available but it also utilizes amino groups which offer different interaction with the analysed components. As can be inferred from the separation obtained, the interaction is stronger with *N,N*-dimethylaniline (much

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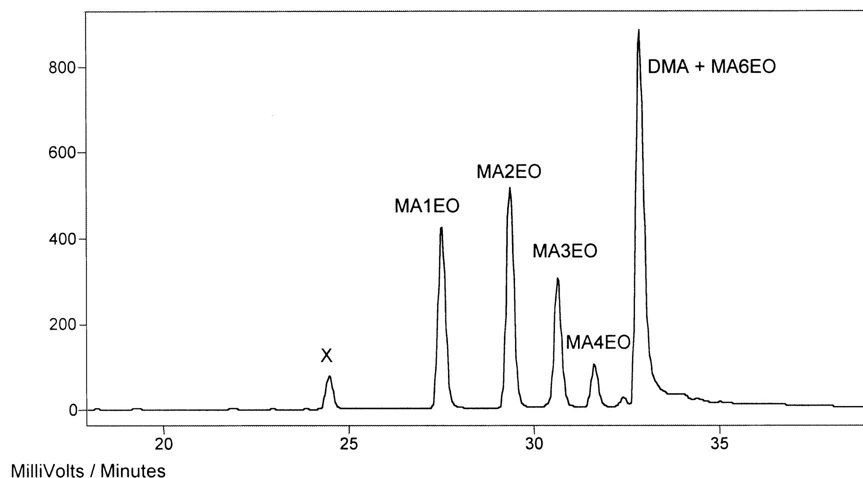

Figure 1. Chromatogram for *N*-methylaniline ethoxylates (MAnEO) obtained from the Purospher C18 column. Flow rate = 0.5 mL/min, while other analytical parameters as provided in the text.

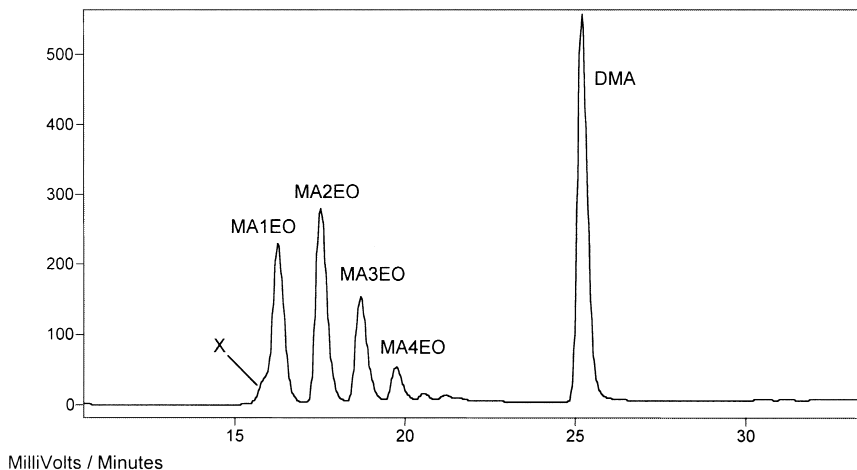

Figure 2. Chromatogram for *N*-ethylaniline ethoxylates (MAnEO) obtained from the "mixed-mode C18/anion" column. Analytical parameters as provided in the text.

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longer retention times) than with aniline derivatives which contain oxyethylene groups (–OH groups and ether bonds –O–).

The "MIXED-MODE" C18/CATION 300A, 150 x 4.6 mm, Alltech (Deerfield, USA) column was employed for the analysis of the same sample in order to verify if it is the amine groups that, are in fact, responsible for the change in retention times. That column has been produced of the same silica but, in addition to C18 groups, it offers carboxyl groups instead of amino groups. Under the analytical conditions employed, i.e., at alkaline pH, carboxyl groups should be present in the form of salts. Thus, they should not be expected to interact with alkaline amino compounds. The column should perform like a regular column with the stationary phase C18. The obtained chromatogram confirms our assumption; initial *N,N*-dimethylaniline undergoes elution together with its derivative which has three oxyethylene segments in its molecule (MA3EO). This proves, that the advantageous change in the retention times available for the "mixed-mode C18/anion" column results from the additional presence of amino functional groups.

Figure 3 compares the chromatograms obtained from the "MIXED-MODE" C18/ANION column for two samples with DMA at different conversion levels, and for a sample produced with *N,N*-diethylaniline (DEA) as a catalyst. The sample with higher conversion contains clearly, less DMA, reduced

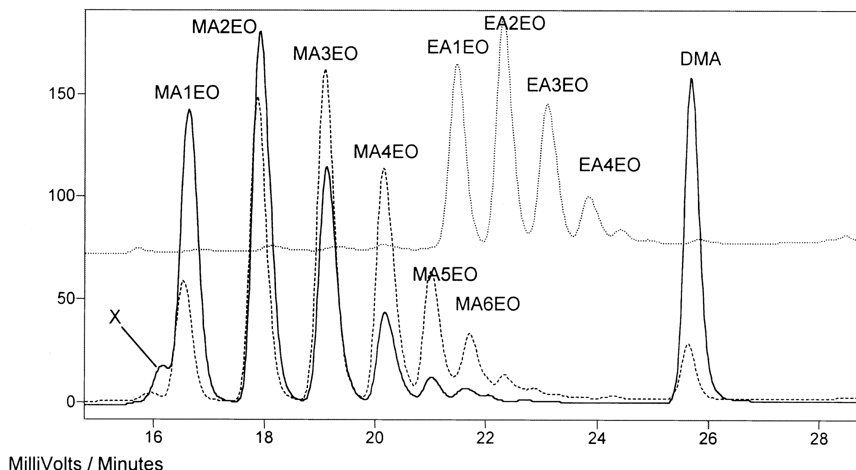

Figure 3. Compared chromatograms for: sample at low conversion of DMA to MAnEO (black, connected line), sample at higher level of conversion (black, dashed line), and sample from converting DEA to EAnEO (grey, dotted line). "mixed-mode C18/anion" column, other analytical parameters as provided in the text.

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shares of lower oxyethylates (MA1EO and MA2EO), while the concentrations of higher oxyethylates are higher.

The peaks of oxyethylates derived from *N,N*-diethylaniline (EAnEO) are eluted at longer retention times which conforms to the mechanism for reversed phase separation. The peak of initial DEA is obtained at 36.6 min., which has not been shown in the figure in order to keep the designations more clear.

Since there were no neat standards available for aniline oxyethylates, UV spectra were taken for the components separated from a typical sample to find the optimum wavelength for the needs of future quantitative analyses. A diode array detector was employed to record the spectra. The spectra for DMA and MAnEO are compared in Figure 4. The local absorption maximum for DMA is 245 nm. All the oxyethylated components in MAnEO revealed their maxima in this region which were very close to each other, at 249 nm. Hence, after the methyl group was replaced with the oxyethylene group the absorption maximum was shifted up by 4 nm. Any extension of the oxyethylene chain resulted in changes in the chromatographic performance of the system.

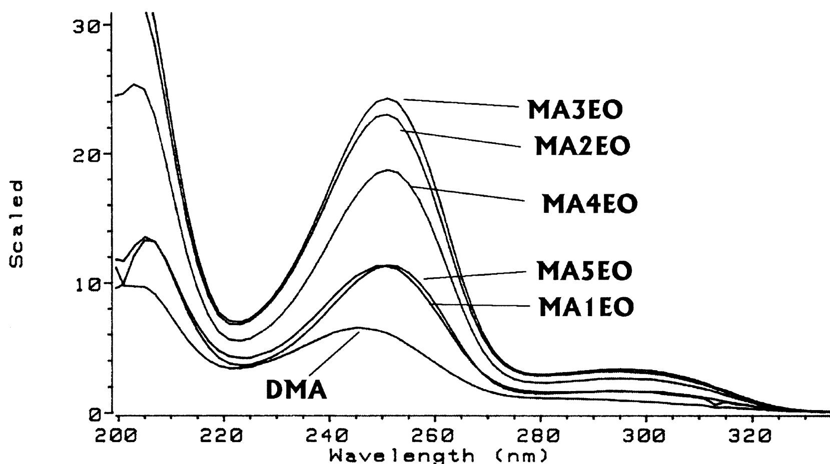

Figure 4. UV spectra for *N,N*-dimethylaniline (DMA) and *N*-methylaniline ethoxylates (MAnEO).

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The situation was much the same for *N,N*-diethylaniline (DEA), where its absorption maximum appeared at 259 nm, while the maxima for the components in EAnEO were at 255 nm, irrespective of the number of oxyethylene segments in the chain. However, in this case, the change of the ethyl group for the oxyethylene group shifted the absorption maximum down by 4 nm.

The absorption intensity profiles presented in Figure 4 are dependent, both on the specific absorption factor, and on the concentration of a component in the sample subjected to separation. However, since it was found that the (changing) length of the oxyethylene chain in the aniline molecule had no effect on the chromophoric group, it seems reasonable that the specific molar absorption of oxyethylates should also be independent on the size of that chain. Thus, the peak areas for the studied oxyethylates are proportional to the corresponding molar concentrations, which is useful in kinetic investigations and in evaluating the distributions for individual homologues. For the analysis of mass concentrations of the discussed components, the calculations are possible while molecular weights are known, and calibration is also possible as initial anilines are available.

In order to simplify the procedure, the detector wavelength of 254 nm was selected from the above-presented analysis of UV spectra as the average value applicable in the investigation of the two considered catalysts. The principal com-

ponents (initial alcohols and their oxyethylates) are invisible at that wavelength. They are eluted from the column very quickly under the analytical adopted conditions and they do not affect the separation of the compounds in question.

Employing a 'double-mode' column made it possible to separate the components of interest and to develop a method with the sensitivity which is satisfactory when the formation of said components and their relative shares have to be observed in the performed study.

REFERENCES

1. J. Poskrobko, J. Wasilewski, E. Dziwiński, H. Poskrobko, E. Milchert, Tenside Surf. Det., **32**, 351-4 (1995).

2. J. Poskrobko, E. Milchert, H. Poskrobko, E. Dziwiński, J. Chem. Tech. Biotechnol., **67**, 84-8 (1996).

3. E. Milchert, J. Poskrobko, H. Poskrobko, Org. Process Res. Dev., **1**, 379-383 (1997).

4. M. Linkiewicz, M. Jaworski, J. Poskrobko, Chem. Anal. (Warsaw), **38**, 149 (1993).

5. J. Poskrobko, M. Linkiewicz, M. Jaworski, Chem. Anal. (Warsaw), **39**, 153 (1994).

6. M. Linkiewicz, H. Poskrobko, Chem Anal. (Warsaw), **38**, 429 (1993).

7. M. Linkiewicz, H. Poskrobko, Chem Anal. (Warsaw), **39**, 93 (1993).

8. M. Linkiewicz, A. Wala-Jerzykiewicz, H. Poskrobko, Chem Anal. (Warsaw), **42**, 599 (1997).

9. B. Schmidt, E. Claus, F. Schmidt, Chem. Techn., **37(2)**, 73-75 (1985).

10. M. Wisniewski, J. Szymanowski, B. Atamanczuk, J. Chromatogr., **462**, 39-47 (1989).

11. M. Wisniewski, J. Szymanowski, E. Dziwiński, Chem.Anal.(Warsaw), **36**, 597-606 (1991).

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