Identification of an Amido-Amine Component in Diethanolamide[1]

MARY ELLEN WITTEKIND and **J. H. BENEDICT**,
The Procter and Gamble Company, Ivorydale Technical Center, Cincinnati, Ohio

Abstract

Diethanolamide products made by the condensation of diethanolamine and fatty acid are known to contain, in addition to the amide, excess diethanolamine, fatty acid soap of diethanolamine and water. In a recent examination of some amide products, a new amido-amine compound was isolated and identified. This compound is formed from two moles of diethanolamine and one mole of fatty acid and is present at levels as high as 10% of amide product.

The amido-amine was isolated by extraction with isobutanol from an acidic solution of the amide. The structure of this new compound was verified by its chemical reactivity and by instrumental analyses. Methods of synthesis were also studied.

Introduction

DIETHANOLAMIDES ARE USED WIDELY in the detergent, cosmetic, and textile industries as detergent actives, viscosity controllers, foam stabilizers, and corrosion inhibitors. There are two types of diethanolamides. The first is the so-called "Ninol-type" or "low-activity" alkanolamide which is prepared by reacting two moles of diethanolamine with one mole of fatty acid. The other is the "high activity" amide made from one mole of methyl ester and one mole of diethanolamine. This report is concerned with the first or "low-activity" diethanolamide.

These amides are complex mixtures and usually contain 55–65% amide, 10–25% diethanolamine soap, 10–25% free amine, and 0–4% water. Several publications (1,4,6) have described various chemical methods for analyzing these products. The chemical method for estimating the amide content involves determining the combined diethanolamine and/or the combined fatty acid content; from these two values one can calculate the apparent amide content. A direct and a relatively rapid method is the infrared (IR) measurement of the amide absorption band near 1625 cm^{-1}. A third technique is the treatment of the sample with monobed ion exchange resin and weighing the eluate which should contain the diethanolamide and any amide ester.

In addition to these methods, procedures for amide ester and amine ester have been described in the literature (1). Because different workers have used different combinations of analytical methods, they have reported different results. Table I lists a comparison of Kroll and Lennon's data (1) and the results of Sanders work (4).

TABLE I
Reported Composition of Diethanolamides

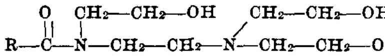
Component	Kroll et al.	Sanders
Amide	49.0%	63.0%
Amine ester	9.5	0
Amide ester	10.5	1.2
Free diethanolamine	28.0	Not reported
"Free" fatty acid	3.0	Not reported

Kroll and Lennon determined the amine ester by extracting the free amine from the original sample and then titrating the residue with acid (1). The titration value was called and calculated as amine ester but was not shown to be an ester. The combined fatty acid and the combined amine values were then corrected for the amine ester and from these numbers the ester amide and the actual amide were calculated.

Sanders used IR spectroscopy to determine the total amount of amide ester using a pure lauric amide ester for calibration (4). He corrected the combined fatty acid value for the ester amide and then calculated the true amide content. He concluded that the methods of Kroll and Lennon must be in error.

We, also, have obtained varying results with different analytical methods. Different apparent compositions were found, depending on whether the sample received a treatment with mixed ion exchange resins before the IR determination. The amide content of a typical sample was 60% with no resin treatment, but appeared to be only 48% upon exposure to ion exchange resins followed by IR measurement. Recovery studies with pure amides indicated that there was no loss during the exposure to the ion exchange resins. However, when a typical sample was passed through a chromatographic column packed with ion exchange resins, 50% of the material was found in the eluate. This agreed fairly well with the IR result on the treated sample but was consistently 2–3% higher than the IR value. Thus, the IR results indicated that some type of amide was present in one analysis and not present in the other.

A new compound, an amido-amine, was isolated from a commercial diethanolamide. The structural formula is:



The "R" group represents coconut fatty acids, or lauric acid, or any other fatty chain that is used for this purpose. The other portion of the amide is a condensation product of two diethanolamine molecules coupled through the terminal end of one and nitrogen of the other. Thus, this amide contains the usual disubstituted amide function plus a tertiary amine group. This molecule will display both functions in any analysis and must be taken into account.

The following discussion will present the method of isolation and our proof of structure for this compound.

Experimental

Isolation

The amido-amine compound was isolated from diethanolamide samples by a solvent-solvent separation. The sample was dissolved in water and adjusted to a pH of 2–3 with 1 N HCl. The amide and fatty acids from the amine soaps were removed by repeated ex-

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traction with a 1:1 mixture of petroleum ether and ethyl ether. Centrifugation was necessary to break the emulsions. The amido-amine was then extracted (as the hydrochloride salt) with isobutanol. Some diethanolamine hydrochloride was also extracted and was removed by evaporating the isobutanol and dissolving the amido-amine in chloroform. The amine hydrochloride was not soluble and was removed by filtration. The amido-amine salt was converted to the free amido-amine by chromatography on an anion exchange resin (hydroxyl form) using a solvent of isopropanol-water (9:1). The eluate was evaporated to dryness and the residue weighed for quantitative measurement.

The amido-amine is a colorless or light yellow oil. Attempts to obtain it in a crystalline form were not successful. The compound is soluble in benzene, ethanol, isopropanol, and warm acetone, but not in hexane. This material is also soluble in water and has foaming properties similar to normal diethanolamide.

Confirmation of Structure

The structure of the amido-amine was verified by chemical and instrumental analyses. The chemical data are presented in Table II. The total nitrogen was determined by Kjeldahl analysis and the amine nitrogen was obtained by nonaqueous titration with perchloric acid (3). The molecular weight was run in a vapor pressure osmometer using methanol as the solvent. The fatty acid content was determined by hydrolysis with 6 N HCl followed by extraction of the fatty acids with petroleum ether. The ionizable chloride content of the amido-amine salt was determined coulometrically. A nonionic determination (6) showed that this material was ionic in nature and not a simple mixture of amide and amine. The experimental values are in good agreement with the calculated values for the proposed structure.

IR spectroscopy also confirmed the proposed structure (see Fig. 1). The absorption peaks typical of amides are evident at 1630, 1470, and 1220 cm^{-1}, and the bands at 1150, 910, and 880 cm^{-1} which are characteristic of diethanolamines. Thus, this IR spectrum indicates that the compound contains both an amine and an amide functional group. This amido-amine, therefore, must involve the condensation of two diethanolamine molecules for each fatty acid.

The amine was isolated by hydrolysis of the amido-amine with 6 N HCl, extraction of the fatty acids, and recovery of the amine from the solution. The structure of the amine was confirmed by NMR based on the ratio of methylenic protons adjacent to hydroxyl groups and the methylenic protons adjacent to nitrogen atoms. The spectrum was completely consistent with the proposed structure. Although this compound has been mentioned a few times in the literature, there is very little chemical information available. To our knowledge, this amine or the amido-amine have not been observed in amides prior to this time.

TABLE II
Chemical Analyses of Amido-Amine

Analyses	Calculated	Found
Amido-Amine		
Total nitrogen, %	7.8	8.1
Amine nitrogen, %	3.9	3.4
Molecular weight	360.0	325.0
Fatty acid content, %	52.0	47.0
Amido-Amine—HCl		
Amine Nitrogen, %	3.5	3.9
Chloride, %	9.0	9.4
Nonionic, %	0.0	0.0

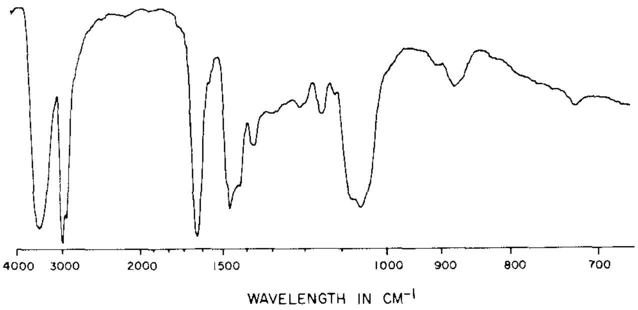


FIG. 1. Infrared spectrum of the amido-amine isolated from a diethanolamide sample.

Discussion

Level of Amido-Amine

The amount of amido-amine found in "Ninol-type" diethanolamides ranged from 1% to 12% in seven commercial samples with most values between 8 and 12%. Although the amido-amine was an appreciable portion of the sample, it seemed to have no effect on performance. A sample was prepared containing about 25% amido-amine and it showed no particular advantage or disadvantage in performance (as judged by cleaning power and sudsing characteristics) over samples containing low levels of this component.

Amides made from the methyl esters of fatty acids contained less than 1% amido-amine.

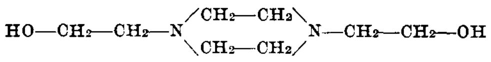
Synthesis

The severity of the processing conditions can affect the level present in the final product. Prolonged heating at elevated temperatures and reduced pressure of a diethanolamide product can cause an increase of the amido-amine from 8% to 25%.

Although we tried to synthesize the amido-amine by known reactions, we were unsuccessful. However, a recent report by a Russian scientist (5) states that the amine can be produced by heating piperazine diethanol dihydrochloride; this reaction merely involves opening the piperazine ring to form the ethylene diamine derivative.

Other Components

Piperazine diethanol has been reported numerous times in the literature (2), but no real proof of its presence has been offered. The structure of this compound is:



$$HO{-}CH_2{-}CH_2{-}N\begin{matrix}/CH_2{-}CH_2\backslash\\ \backslash CH_2{-}CH_2/\end{matrix}N{-}CH_2{-}CH_2{-}OH$$

The material results from the condensation of two molecules of diethanolamine and has two tertiary amine functions. A sample of this compound obtained from K and K Laboratories was titrated quantitatively with perchloric acid in a nonaqueous system. Two inflections in the titration curve were obtained, one for each amine function in the molecule. The second break or inflection was found to be satisfactory for determining the level of piperazine diethanol in typical amide samples. Known amounts of piperazine diethanol were added to known amide samples and could be detected at levels above 3%. Examination of regular samples showed no piperazine diethanol. It is concluded that no significant quantity of this com-

TABLE III
Average Composition of Diethanolamides

Component	Percent
Diethanolamide	48
Monoethanolamide	2
Amido-Amine	10
Amide ester	1
Free diethanolamine	26
Amine soap	11
Water	2
	Total—100%

pound is present in commercial diethanolamides.

Another compound that was also detected in the commercial samples was monoethanolamide. Approximately 2% monoethanolamide was found by isolating the amides through ion exchange chromatography and then analyzing these amides by gas chromatography. Examination of diethanolamine receipts showed approximately 5% monoethanolamine to be present. Therefore, it is not surprising to find monoethanolamide in the product.

Composition of Diethanolamide

Based upon all of the observations discussed before, a new overall composition for diethanolamides is presented in Table III. The amide level determined by IR spectroscopy *without* ion exchange resin treatment will be approximately 61%. However, IR determinations that are performed on ion exchange resin treated samples will show 48–49% amide. The monoethanolamide has a slightly different amide absorption in the infrared region of 6.1–6.2 μ, and therefore is not included in the IR measurement for DEA. The nonionic value, which is obtained by chromatography on an ion exchange column, is approximately 51% because the nonionic contains both the monoethanolamide and the diethanolamide as well as any amide ester. Chemical analyses for combined diethanolamine and fatty acids will give a calculated amide content of approximately 61%.

The presence of the amido-amine can also explain the results of Kroll and Lennon (1) which they interpreted as amine ester. In their procedure the free amine is removed from the sample by extraction. Then other amines in the remaining sample are titrated; they assumed that this was amine ester but, in fact, it was most likely the amido-amine. We agree with the work of Sanders (4) and also Trowbridge which shows that amine esters readily convert to amides at room temperature and, therefore, no amine ester should be present. When one uses these new interpretations for the actual components present, the agreement of results obtained by Kroll et al. and by Sanders is surprisingly good. Thus, the amido-amine explains many of the anomalies that have occurred previously.

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