

## Technical Notes

### By-Products of Ethoxylation of Diethylethanolamine and Its Solutions in Methanol

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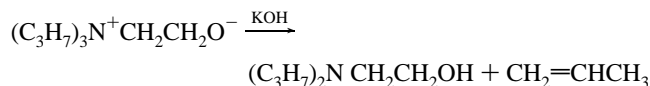
#### Abstract:

Major products and by-products of the ethoxylation of diethylethanolamine and its solutions in methanol have been identified. Through gas chromatography and mass spectrometry, it has been found that by-products correspond to ethyldiethanolamine and its succeeding ethoxylates. In methanol ethoxylation, diethylethanolamine acts as a catalyst and also itself undergoes ethoxylation, forming two types of products.

#### Introduction

During the industrial ethoxylation of simple alcohols (methyl, ethyl, *n*-butyl) in the presence of triethylamine as a catalyst, alcohol ethoxylates  $R(OCH_2CH_2)_nH$ , where  $R = CH_3$ ,  $C_2H_5$ , and  $C_4H_9$ , ethylene glycol, products of its ethoxylation, polyglycols  $HO(CH_2CH_2O)_nH$ , and products of triethylamine transformation are formed. The last compounds have been identified<sup>1</sup> as diethylpolyethoxyethanolamines (DPEA),  $(C_2H_5)_2N(CH_2CH_2O)_nH$ , where  $n = 1, 2, 3 \dots$ , and denoted respectively as A1, A2, A3, ...  $A_n$ . They were identified by comparison of retention indices and mass spectra of succeeding DPEA ( $A1 \rightarrow A_n$ ) from the diethylethanolamine (DEA) ethoxylation process and ethoxylation of alcohols in the presence of triethylamine.

Further investigations<sup>2</sup> showed that trialkylamine and ethylene oxide form a quaternary ammonium alkoxide which, through an elimination reaction, results in the formation of an alkene and a dialkylethanolamine, e.g., during the ethoxylation of tripropylamine:



This work shows that products of pure DEA (A1) ethoxylation contain DPEA A2, A3, and A4 and a number of new unidentified compounds. Presumably they result from DEA transformations similar to the previously found transformations of triethylamine<sup>1</sup> and tripropylamine.<sup>2</sup> To confirm the formation of these compounds in the products of methanol ethoxylation in the presence of DEA, the

ethoxylation of 5 and 10% solutions of DEA in methanol was carried out. Thus experiment shows that methanol ethoxylation proceeds in the presence of DEA as the catalyst (peaks M1  $\rightarrow$  M3), giving products of its transformation (peaks A1  $\rightarrow$  A4) and new unidentified compounds (DA2  $\rightarrow$  DA5) (Figure 1). The ethoxylation of methanol in the presence of 0.5 wt % DEA (in relation to alcohol) proceeded in a similar way; 0.5% is the concentration of tripropylamine applied in industrial processes for simple alcohol ethoxylation.

By-products of DEA transformations (both A1  $\rightarrow$  A4 and DA2  $\rightarrow$  DA5) found in commercial ethoxylated alcohols influence their properties and application as brake fluids, antifreezes for aviation fuels, solvents, and diluents.

#### Experimental Section

**Materials.** The following reagents were used in the experiments: diethylethanolamine, pure (Merck-Schuchardt); methanol, technical grade (Chemical Manufactures Oświęcim (according to PN-74/C-97905)), ethylene oxide ("Petrochemia" Płock (according to BN-74/6026-41)); and distillation fractions of methyl alcohol ethoxylates (ICSO Chemical Production, Blachownia, Poland).

**Identification of Components by Gas Chromatography.** A Hewlett-Packard gas chromatograph, type 5890 II, attached to a mass detector MSD 5971 A was used for identification of DA1  $\rightarrow$  DA5 compounds. Chromatographic separation<sup>3</sup> was performed on an Ultra 2 capillary column (Hewlett-Packard, 0.52  $\mu$ m thick methylsilicone phase containing 5% of phenyl groups) working in the temperature range 50–310 °C with a temperature gradient of 8 °C/min. The injector and detector temperature was 310 °C. Hydrogen flowing at 2 cm<sup>3</sup>/min was used as a carrier gas. The injection split was 1:100, and sample volume varied from 0.1 to 0.3  $\mu$ L.

The mass detector was operated under the following conditions: transfer line temperature 280 °C, ion source temperature 170 °C, ionization energy 70 eV, ion accelerating voltage 1700 V, the *m/e* range 10–550 of atomic weight units.

The quantitative analysis (GC) of the ethoxylation products was performed by the method of internal standard (Table 1). Correction coefficients of A4  $\rightarrow$  A6 compounds were

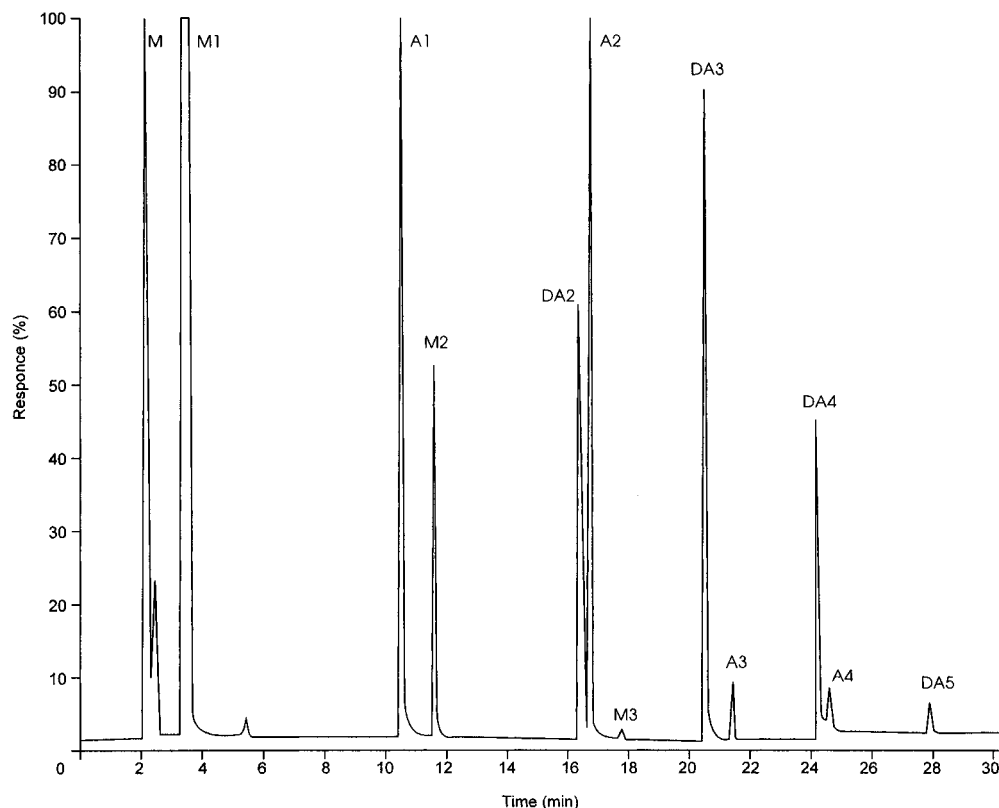
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(1) Poskrobko, J.; Wasilewski, J.; Dziwiński, E.; Poskrobko, H.; Milchert, E. *Tenside, Surfactants, Deterg.* **1995**, 32, 351.

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

(3) Poskrobko, J.; Linkiewicz, M.; Jaworski, M. *Chem. Anal.* **1994**, 39, 153.



**Figure 1.** Chromatogram of the products of ethoxylation of a 10% solution of diethylethanolamine in methanol: M, methanol; M1, methyl ether of ethylene glycol,  $\text{CH}_3\text{OC}_2\text{H}_4\text{OH}$ ; M2, methyl ether of diethylene glycol,  $\text{CH}_3\text{O}(\text{C}_2\text{H}_4\text{O})_2\text{H}$ ; M3, methyl ether of triethylene glycol,  $\text{CH}_3\text{O}(\text{C}_2\text{H}_4\text{O})_3\text{H}$ ; A1, diethylethanolamine,  $(\text{C}_2\text{H}_5)_2\text{NC}_2\text{H}_4\text{OH}$ ; A2, diethyl(2-(2-hydroxyethoxy)ethyl)amine,  $(\text{C}_2\text{H}_5)_2\text{N}(\text{C}_2\text{H}_4\text{O})_2\text{H}$ ; A3, diethyl(2-(2-(2-hydroxyethoxy)ethoxy)ethyl)amine,  $(\text{C}_2\text{H}_5)_2\text{N}(\text{C}_2\text{H}_4\text{O})_3\text{H}$ ; A4, diethyl(2-(2-(2-(2-hydroxyethoxy)ethoxy)ethoxy)ethyl)amine,  $(\text{C}_2\text{H}_5)_2\text{N}(\text{C}_2\text{H}_4\text{O})_4\text{H}$ ; DA2  $\rightarrow$  DA5, ethyldiethanolamine and products of its ethoxylation.

**Table 1.** Composition (wt %) of the products of ethoxylation of diethylethanolamine (A1) and its 10% solution in methanol

component	10% soln of A1 in methanol	A1
M	66.7	
M1	17.8	
M2	1.4	
A1	5.3	18.0
A2	2.2	28.1
A3	0.2	14.1
A4	0.0	4.3
A5	0.0	1.0
A6	0.0	0.2
DA2	1.5	1.0
DA3	2.2	5.1
DA4	1.2	5.3
DA5	0.2	5.0
DA6	0.0	2.3

assumed as for A3 and for compounds DA4  $\rightarrow$  DA6 as for DA3.

**Ethoxylation Procedures.** *Ethoxylation of Diethylethanolamine.* Diethylethanolamine (2.14 mol 250 g) was placed in a steel autoclave equipped with a stirrer, heating jacket, and cooling coil. After the reaction temperature (135–140 °C) was reached, the heating was turned off and 6.4 mol (281 g) of ethylene oxide was added gradually. The rate of oxide addition and the flow rate of cooling water were adjusted to maintain the reaction temperature constant and pressure in the range 0.2–0.5 MPa. When feeding was

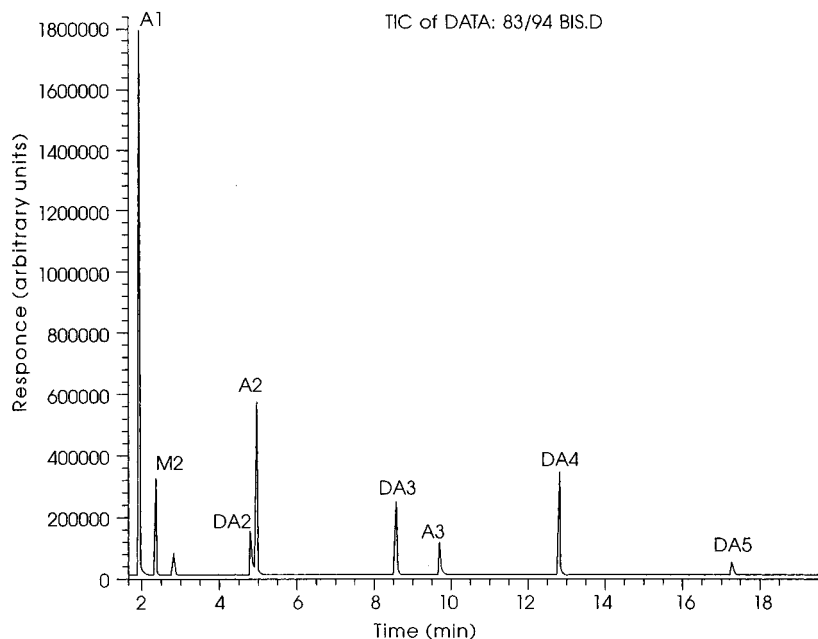
completed, the ethylene oxide to DEA molar ratio was 3:1 and the reaction time 3.3 h.

*Ethoxylation of 10% Solution of DEA in Methanol.* As previously, 0.26 mol (31 g) of DEA and 8.4 mol (269 g) of methanol were placed in an autoclave, heated to 85 °C, followed by gradual addition of 3.02 mol (132 g) of ethylene oxide. The addition time was 3 h. The process was carried out at 85 °C and under 0.2–0.4 MPa. The molar ratio of ethylene oxide to DEA to methanol was 12:1:32. The ethoxylation of a 5% solution of DEA in methanol was performed in a similar way.

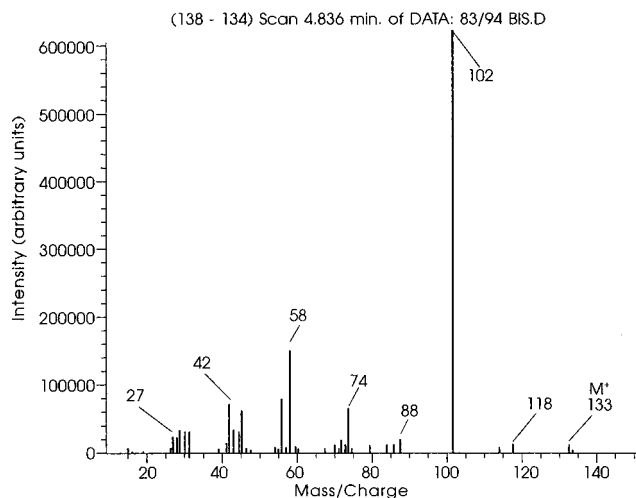
## Results and Discussion

Figure 1 shows the chromatogram of the ethoxylation products of a 10% solution of DEA in methanol, namely, compounds resulting from ethoxylation of methanol (peaks M1  $\rightarrow$  M3), from ethoxylation of DEA (peaks A2  $\rightarrow$  A4) and unidentified components (peaks DA2  $\rightarrow$  DA5). The retention times of these last compounds (peaks DA2  $\rightarrow$  DA5) are identical to those obtained during the ethoxylation of pure DEA and a 5% solution of DEA in methanol. Therefore it is most probable that these compounds are the products of DEA transformations. The composition of the products of a 10% solution of DEA in methanol and pure DEA ethoxylation is shown in Table 1.

Additional by-products DA2  $\rightarrow$  DA5 also appear in small quantities in industrial processes for ethoxylation of alcohols in the presence of triethylamine. Our investigations confirmed the presence of DA1 and DA2 peaks in fractions thickened by distillation of ethoxylates of methyl alcohol



**Figure 2.** Section of the chromatogram of 10% diethylethanolamine solution ethoxylation products recorded as the total ion current (TIC).



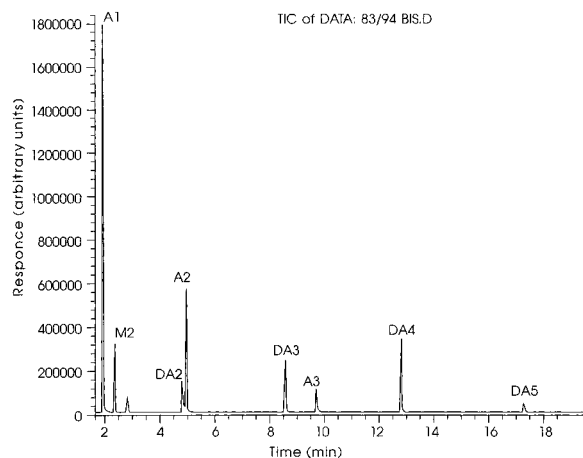
**Figure 3.** Mass spectrum of DA2,  $C_2H_5N(C_2H_4OH)_2$ , ethyldiethanolamine.

obtained from ICSO Chemical Production, Blachownia, Poland. The ethoxylation was carried out in the presence of triethylamine as a catalyst (1 wt % vs methyl alcohol). In these processes DEA (A1) and DPEA ( $A2 \rightarrow A_n$ )<sup>2</sup> are formed, and their concentrations in distillation fractions are 3.0–0.01 wt %.

#### Identification of Components by the GC/MS Method.

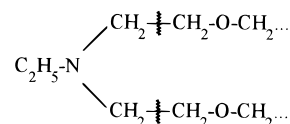
The structure of additional by-products  $DA2 \rightarrow DA5$  was confirmed using chromatography/mass spectrometry (GC/MS). Figure 2 shows a section of the chromatogram of ethoxylation of the 10% solution of DEA in methanol, recorded as the total ion current (TIC). Figures 3–6 show mass spectra obtained at retention times corresponding to successive peaks of  $DA2 \rightarrow DA5$ .

The spectra feature very weak molecular ions ( $M^+$ ), along with one or two peaks of high intensity. The character of the spectra is similar to that obtained by Szymanowski and



**Figure 4.** Mass spectrum of DA3,  $C_2H_5N(C_2H_4OH)[(C_2H_4O)_2H]$ , ethyl-*N,O*-bis(2-hydroxyethyl)ethanolamine.

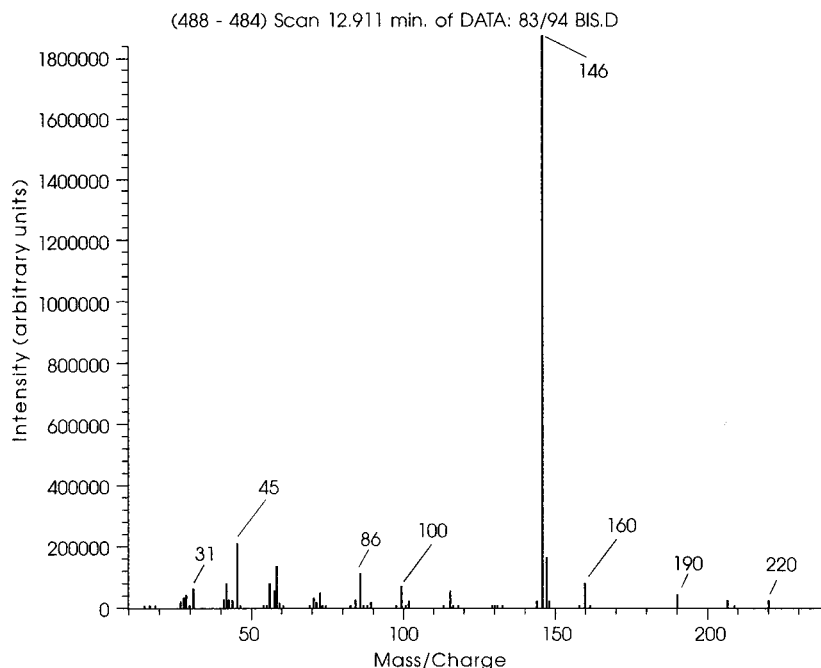
Szewczyk<sup>4,5</sup> for the products of the ethoxylation of aliphatic amines. Mass spectra of alkylamines show a specific main ion resulting from cleavage of a C–C bond in the  $\alpha/\beta$  position with respect to the nitrogen atom. If there are an alkyl and a poly(ethoxylene) chain in a molecule, bond cleavage occurs mainly in the poly(ethoxylene) chain. If there are two poly(ethoxylene) chains in a molecule, the probability of chain cleavage is similar for both of them:



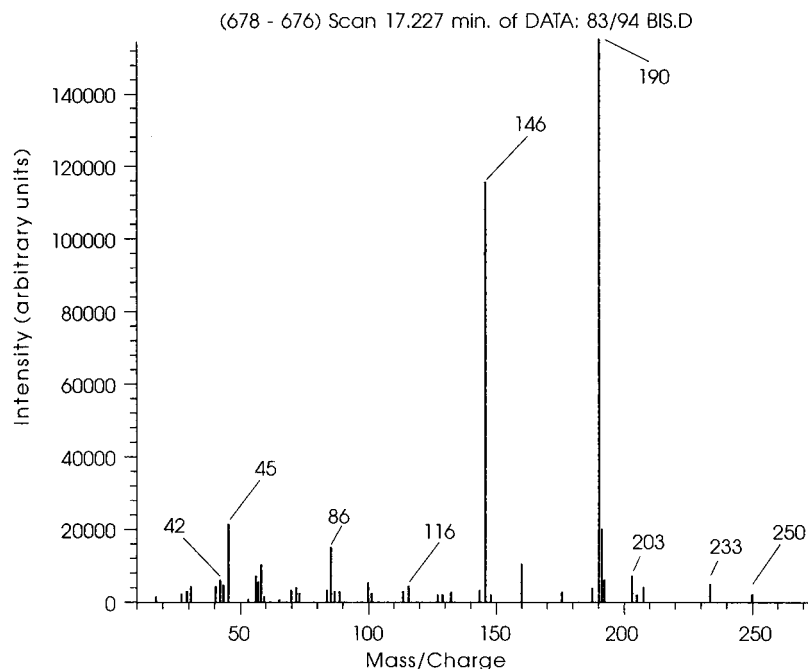
Thus the spectrum of the DA2 fraction (Figure 3) with main peak at  $m/e$  102, of high intensity, corresponds to the  $[(C_2H_5N(CH_2)(C_2H_4OH))]^+$  ion; of lower intensity is the

(4) Szymanowski, J.; Szewczyk, H.; Jerzykiewicz, W. *Tenside Deterg.* **1981**, 18, 130.

(5) Szymanowski, J.; Szewczyk, H.; Hetper, J.; Beger, J. *J. Chromatogr.* **1986**, 35, 183.



**Figure 5.** Mass spectrum of DA4,  $\text{C}_2\text{H}_5\text{N}[(\text{C}_2\text{H}_4\text{O})_2\text{H}]_2$ , ethylbis(2-(2-hydroxyethoxy)ethyl)amine.



**Figure 6.** Mass spectrum of DA5,  $\text{C}_2\text{H}_5\text{N}[(\text{C}_2\text{H}_4\text{O})_2\text{H}][(\text{C}_2\text{H}_4\text{O})_3\text{H}]$ , ethyl(2-(2-hydroxyethoxy)ethyl)(2-(2-(2-hydroxyethoxy)ethoxy)-ethyl)amine.

molecular ion ( $\text{M}^+$ ),  $m/e$  133. The identified compound corresponds to ethylbis(2-hydroxyethyl)amine:  $\text{C}_2\text{H}_5\text{N}(\text{CH}_2\text{-CH}_2\text{OH})_2$ .

In the DA3 spectrum (Figure 4), two high-intensity peaks are observed at  $m/e$  102 and 146. The peak at  $m/e$  146 corresponds to the  $[(\text{C}_2\text{H}_5\text{N}(\text{CH}_2)(\text{C}_2\text{H}_4\text{O})_2\text{H})]^+$  ion. This results from the difference in the relative lengths of poly(ethoxylene) chains. Corresponding compounds differ in one molecule of ethylene oxide (mass 44), and the identified compound is thus ethyl-*N,O*-bis(2-hydroxyethyl)ethanolamine.  $\text{C}_2\text{H}_5\text{N}(\text{C}_2\text{H}_4\text{OH})[(\text{C}_2\text{H}_4\text{O})_2\text{H}]$ . In this spectrum a molecular ion ( $\text{M}^+$ ) at  $m/e$  177 is observed.

Compound DA4 (Figure 5) has again only one intense peak, at  $m/e$  146, showing that the poly(ethoxylene) chains

have the same length, and the compound is thus ethylbis(2-(2-hydroxyethoxy)ethyl)amine:  $\text{C}_2\text{H}_5\text{N}[(\text{C}_2\text{H}_4\text{O})_2\text{H}]_2$ .

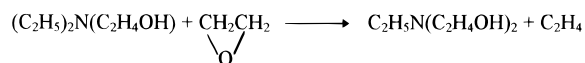
The next compound, DA5 (Figure 6), with two intense peaks, at  $m/e$  146 and 190, has poly(ethoxylene) chains of different lengths and is thus ethyl(2-(2-hydroxyethoxy)-ethyl)(2-(2-(2-hydroxyethoxy)ethoxy)ethyl)amine:  $\text{C}_2\text{H}_5\text{N}[(\text{C}_2\text{H}_4\text{O})_2\text{H}][(\text{C}_2\text{H}_4\text{O})_3\text{H}]$ . The peak at  $m/e$  190 corresponds to  $[(\text{C}_2\text{H}_5\text{N}(\text{CH}_2)(\text{C}_2\text{H}_4\text{O})_3\text{H})]^+$ .

In spite of the absence of molecular ions for compounds DA4 and DA5, and very low intensity molecular ions of DA2 and DA3, specific for ethoxylation products, specific peaks of high intensity allow for the explicit determination of the structure of the compounds under investigation, including the determination of poly(ethoxylene) chain length. Also,

additional by-products are ethylpolyethoxyethanolamines.

### Conclusions

During the ethoxylation of DEA and methanol in the presence of DEA, the addition of ethylene oxide to DEA (*An* products) and to methanol (*Mn* products) proceeds. Along with these reactions, ethyldiethanolamine and the products of its ethoxylation (*DAn* products) are formed. The formation of these compounds can be explained by ethylene elimination and addition of ethylene oxide according to the reaction



During industrial ethoxylation of alcohols in the presence of triethylamine as a catalyst, DEA, the products of its further transformation (ethyldiethanolamine) and products of its ethoxylation are formed.

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