REACTIONS OF ETHOXYLATES OF ETHYLENEDIAMINE AND PIPERAZINE OVER ZSM-5 ZEOLITE

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Abstract

The cyclisation of ethoxylates of ethylenediamine (EDA) and piperazina (PIP) over ZSM-5 zeolite to 1,4-diazabicyclo[2,2,2]octane (TEDA) was studied. It was found that monoethoxylates of EDA and PIP provide significantly higher yield then any of the bisethoxylates investigated. All of tested compounds provide over the zeolite catalyst unsaturated cyclic compounds, mostly pyrazine derivatives.

*Keywords:* ZSM-5 zeolite; cyclisation of ethoxylates; pyrazines formation.

1. Introduction

One of the most required catalysts for the synthesis of polyurethanes is 1,4-diazabicyclo [2,2,2] octane (TEDA) [1]. The TEDA production process is based on acid-catalysed cycling of suitable amines in gaseous phase [2] or liquid one [3]. The amines suitable for the TEDA production are hydroxyethyl or aminoethyl derivatives of piperazine, ethylenediamine, and aminoethanol. At present technologies are preferred, which are based on a gaseous phase reaction over acidic heterogeneous catalyst, namely of the pentasil structure [4] of ZSM-5. Over this type of catalyst, which might be modified applying various procedures [5], the TEDA yield at the level of 60 to 90 % may be attained depending on the raw material used.

The production of TEDA is dealt with our patent of 1998 [6]. The technology is based on the cycling of ethoxylates of ethylenediamine (EDA) and piperazine (PIP) in gaseous phase over a catalyst having the pentasil structure. The process has two stages. In the first, non-catalytic one EDA and ethylene oxide (ETOX) reacts forming N-(2-hydroxyethyl)-ethylenediamine (HEEDA), which proceeds into the second stage where it is cycled into PIP. Piperazine is returned into the first stage where it reacts with another molecule of ETOX giving N-(2-hydroxyethyl)piperazine (HEPIP), which in the second reaction stage gives TEDA (see scheme 1). This scheme is very simplified, ethoxylations to higher degrees may also occur, HEEDA and HEPIP give also other products over an acidic catalyst than those given in the scheme 1. The reaction of HEEDA over the zeolite HZSM-5 was studied by Subrahmanyam et al. [7] and they state PIP to be the only important product. As it will be demonstrated in this paper HEEDA may provide directly TEDA and undergo decomposition reactions.

The most important by-products of the ethoxylation reaction are N,N'-bis(2-hydroxyethyl) ethylenediamine (BIS-LIN), N,N-bis(2-hydroxyethyl)ethylenediamine (BIS-TER), and N,N'-bis(2-hydroxyethyl)piperazine (BHEPIP). These compounds may also be converted into TEDA. BIS-LIN and BIS-TER are given as raw materials for the TEDA synthesis in the Guseva at al. patent [8] of 1976. BHEPIP is mentioned as raw material namely concerning the liquid phase TEDA synthesis [9]. In our laboratory's paper [10], which dealt with studies of the EDA and PIP ethoxylation kinetics, it was found that rates of formation of HEEDA, BIS-LIN, and BIS-TER are in the ratio 1 : 0.38 : 0.48, respectively. The rates of formation of HEPIP and BHEPIP are in the ratio 1 : 0.31. It is obvious from the results, that even at a low conversion of EDA and PIP there will be bisethoxylates present at significant amount and thus it is appropriate to investigate behaviour of these compounds over the catalyst ZSM-5. In this paper EDA and PIP compounds are compared to their mono- and bisethoxylates in terms of the TEDA yield they provide and the formation of by-product compounds, which may be further converted into TEDA.
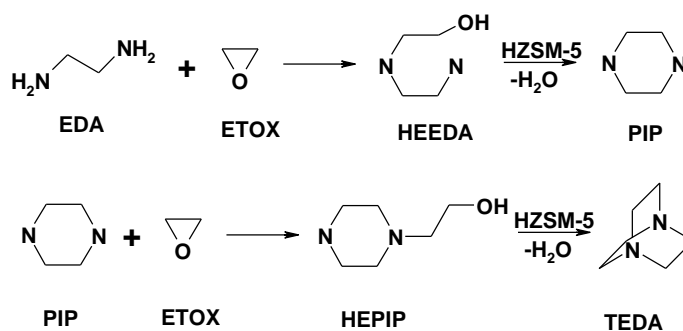
Scheme 1 Application of ethylene oxide in the TEDA synthesis

2. Experimental

2.1. Chemicals

Ethylenediamine (99%), piperazine (98 %), and N-(2-hydroxyethyl)piperazine (97%) were obtained from Sigma-Aldrich Co. Ethylene oxide (Linde a.s., Czech Republic) was used without any purification directly from a cylinder. Hydroxyethyl derivatives of EDA were obtained by the EDA ethoxylation (EDA conversion 90 %) and subsequent separation by means of distillation and crystallisation. HEEDA was obtained as a substance 99.9 % pure having boiling point 114°C at pressure 0.5 kPa. In the fraction with boiling point 150-190°C at pressure 0.5 kPa a mixture composing of 55 % BIS-LIN and 45 % BIS-TER was acquired. BIS-LIN, 99.9% pure, was obtained from the mixture by repeated crystallisation from methanol. The distillation of mother liquor gave a fraction with boiling point 165-167°C at pressure 0.5 kPa containing 98.5 % BIS-TER. N,N'-bis(2-hydroxyethyl)piperazine was obtained through the HEPIP ethoxylation (HEPIP conversion 80 %) and separation by crystallisation. Pure BHEPIP (99,9%) was prepared by recrystallisation from methanol.

Zeolite ZSM-5 with module Si/Al = 36.5 obtained from VÚAnCh, Ústí nad Labem, Czech Republic was used as a catalyst. The catalyst was used in the extruded form (extrudates 1.6 mm in diameter and 5-7 mm in length) with SiO_2 (25 wt%) as a binder.

2.2. Catalyst test

Experiments were carried out in a tube reactor with a fixed catalyst bed. The reactor was 70 cm long and its inner bore was 1.4 cm. Temperature was measured by means of a thermocouple, which was located in a thermowell (4 mm) located in the reactor axis. The first 50 cm of the reactor were employed as an evaporator and thus they were filled with a ceramic packaging, then 10-cm-long layer of catalyst (6.5 g catalyst) followed. The reactor end was filled with ceramic packing again. The evaporator and the catalyst bed were heated separately. It was managed to maintain the temperature selected along the catalyst layer within the range of 2°C. After the reactor there was a sampling vessel immersed in ice bath. The raw materials were fed into the reactor by means of a piston pump.

The catalyst was activated in the dry air flux (75 L/h) at temperature gradient 5°C/min up to temperature 400°C for 3 hours. Reaction temperature of every experiment was 350°C. Aqueous solutions of molar concentration of 10 % amine were used as raw material. In the case of PIP only the concentration employed was lower, 7.7 %, for the sake of the lower solubility thereof.

2.3. Analytical methods

Quantitative analysis of reaction mixtures was carried out by means of the gas chromato-graph SHIMADZU-GC9 with a FI detector. The capillary column DB-5 (30 m x 0.5 mm, film 1 µm) was employed. Nitrogen served as carrier gas. Mass balance at the inlet and outlet of the reactor was performed. The difference in weight at the inlet and outlet did not exceed 1 %. Samples withdrawn were homogenised by methanol and analysed using the internal normalisation method. Correction factors were determined pursuant to standards of pure compounds. Because macro-molecular compounds, or potentially gaseous products, may be formed, which cannot be determined by means of gas chromatography, for each sample the C index was calculated, value of which gives the extent of reactions producing such compounds. The C index is defined as the ratio of the sum of molar amounts of carbon in products identified by means of gas chromatography in the reaction mixture and the

molar amount of carbon in the raw material fed. The index may reach the value of 1 as maximum when no non-detectable compound is formed. Qualitative analysis of reaction mixtures was carried out by means of gas chromatograph GCMS-QP 2010 SHIMADZU equipped with a MS detector. The capillary column DB-5 (60 m x 0.32 mm, film 1 µm) and helium, as carrier gas, were employed.

3. Results and discussion

3.1. Ethylenediamine and its hydroxyethyl derivatives

Out of all the compounds investigated EDA demonstrated the highest selectivity for the TEDA and PIP formation (table I.). At 80 % conversion the aggregate of theoretical yields of PIP and TEDA is 90 %. The assumed reaction pathway of the formation of TEDA and PIP from EDA is shown in scheme 2.
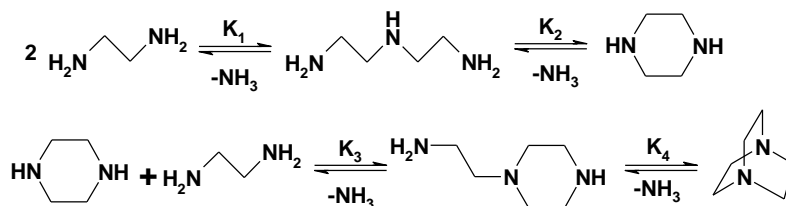
Scheme 2. The reaction pathway for the TEDA synthesis from ethylene diamine

Although diethylenetriamine (DETA) and N-aminoethylpiperazine (AEPIP) belong to intermediates, AEPIP was found at a small concentration, DETA was not detected at all. Equilibrium constants were calculated for the reaction in scheme 2 under temperature 350°C and pressure 101.325 kPa using the database of the Aspen Plus software. Values of equilibrium constants for the given conditions are as follows:

K_1= 14
K_2 = 21120875
K_3 = 0.92
K_4 =665997

It is generally known that reactions over zeolites occur under a strong effect of diffusion however in this case the reaction mixture composition may be influenced by thermodynamics because of the huge difference in equilibrium constant values. The formation of cyclic compounds is so much favoured that the reaction mixture contains PIP and TEDA as main products while AEPIP is found at merely a small concentration and DETA is not found at all.

Table 1. Weight concentration of the compounds in the reaction mixture for different conversion of EDA. Concentration of EDA in the feed water solution was 28.8 % wt.

WHSV [h$^-$]	4.6	2.8	1.7	0.9
Conversion	36.7	49.6	62.7	80
EDA	18.40	14.53	10.88	5.88
PIP	3.22	4.14	5.33	6.44
EPYR*	0.05	0.09	0.12	0.20
EPIP	0.05	0.09	0.14	0.24
TEDA	1.75	2.70	4.35	7.44
AEPIP	0.11	0.12	0.11	0.09
C index	0.90	0.87	0.89	0.94

*EPYR included also 2,3-dimethylpyrazine portion

By-products are, first of all, N-ethylpiperazine (EPIP) and pyrazines (PYR) represented mainly by ethylpyrazine (EPYR) and 2,3-dimethylpyrazine (DMPYR). The formation of pyrazine was described by Srinivas et al. [11] in their paper. They assume direct dehydrogenation of the piperazine ring producing pyrazines and hydrogen. This mechanism is however little likely over an acidic catalyst. Reichle in his paper [12] employed hydrogen as a carrier gas to suppress the pyrazines formation and detected no positive effect. The reaction pathways of the formation of EPIP and pyrazines were explained in our paper [13] as a sequence of elimination, aldolisation, and hydrogen transfer reactions (scheme 3).
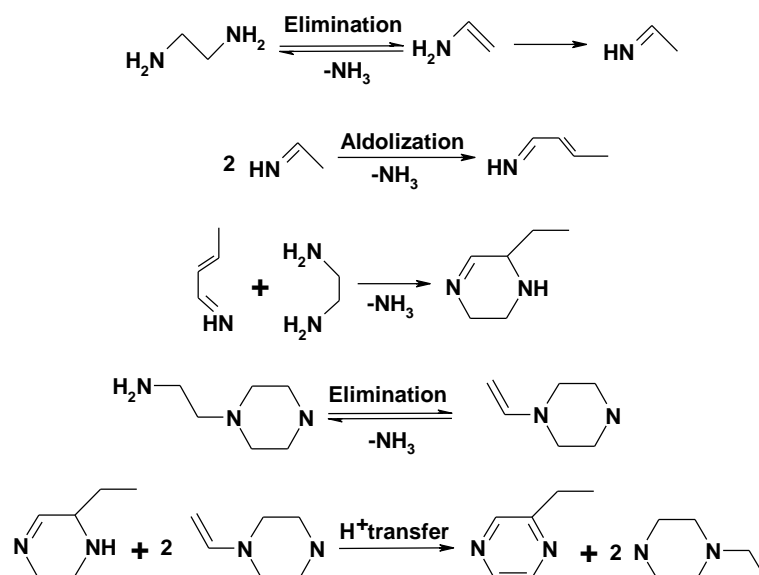
Scheme 3. Example of pyrazines formation by the elimination, aldolisation, and hydrogen transfer reactions

Monoethoxylated ethylenediamine (HEEDA) over the catalyst ZSM-5 undergoes (table 2.), except for the expected reaction into PIP, also decomposition reactions yielding EDA and 2-aminoethanol (AE), and further formed compounds are TEDA, AEPIP, BHEPIP, N-hydroxyethyl-N`-aminoethylpiperazine (HEAEPIP), and 1,2-bispiperazinoethane (BPIPE). Results are summarised in Table 2. HEEDA provides a lower yield of TEDA than EDA. By-products from the reaction mixture may be further converted into TEDA which increases yield. Besides the compounds discussed in the paper, this is first of all AE, which has been subject to many papers [14, 15] dedicated to the TEDA preparation. More pyrazines are also formed from HEEDA. Their amount based to the TEDA produced is substantially higher here compared to experiments with EDA. It is probably caused by a higher tendency to the elimination of hydroxy group. Some papers dealing with the preparation of pyrazines over ZSM-5 give AE to be a suitable raw material [16]. The formation of macro-molecular compounds from HEEDA is higher in the case of EDA, which follows from the C index values comparison. In the reaction mixture no morpholine was detected, as potential product of HEEDA or AE etherification.

Table 2. Weight concentration of the compounds in the reaction mixture for different conversion of HEEDA. Concentration of HEEDA in the feed water solution was 41.2 % wt.

WHSV [h$^-$]	6.3	4.8	2.8	1.8
Conversion	37.8	50.1	75	85.8
EDA	1.31	1.49	2.08	2.51
AE	1.52	1.62	2.09	2.32
PIP	2.41	2.61	3.68	4.45
EPYR	0.10	0.12	0.27	0.49
EPIP	0.15	0.18	0.40	0.60
TEDA	2.12	2.40	3.60	4.66
HEEDA	27.92	21.29	10.30	5.88
AEPIP	1.99	2.14	2.49	3.04
BHEPIP	0.50	0.80	0.49	0.54
HEAEPIP	0.70	0.67	0.64	0.63
BPIPE	0.74	0.75	0.99	1.09
C index	0.92	0.85	0.73	0.73

Reactions of bis-hydroxyethyl derivatives of EDA over ZSM-5 are much less selective, which is obvious from the comparison of their C index values with those of EDA and HEEDA. BIS-LIN undergoes mostly cycling to HEPIP and TEDA and furthermore decomposition yielding AE and HEEDA. The PIP yield in this case is low and comparable to the amounts of PYR and EPIP formed. The important compound in the reaction mixture is N-hydroxyethyl-

N'-ethylpiperazine (EHEPIP). The composition of reaction mixtures from experiments with BIS-LIN is summarised in Table 3.

Table 3. Weight concentration of the compounds in the reaction mixture for different conversion of BIS-LIN. Concentration of BIS-LIN in the feed water solution was 50 % wt.

WHSV [h⁻]	7.7	4.9	3.2
Conversion	45.7	81.7	92
AE	0.43	0.79	1.16
PIP	0.20	0.37	0.60
EPYR	0.09	0.17	0.34
EPIP	0.12	0.21	0.41
TEDA	1.11	2.11	3.50
HEEDA	0.33	0.38	0.59
HEPIP	5.76	9.11	11.56
EHEPIP	0.30	0.55	0.91
BIS_LIN	27.37	9.39	4.06
BHEPIP	0.37	0.88	0.79
BPIPE	0.12	0.18	0.44
C index	0.74	0.51	0.55

In the reaction BIS-TER mostly undergoes cycling to HEPIP and TEDA, while decompositions to AE and HEEDA were not observed in this case. Table IV provides the summary of experimental results. It was found, comparing BIS-LIN and BIS-TER at the same catalyst load (WHSV 3.2 h⁻¹), that the BIS-LIN conversion is higher (92 %) than conversion of BIS-TER (66.1 %). This may be caused either by different rate of diffusion in the pores of the zeolite ZSM-5, or by also higher rate of decomposition reactions of BIS-LIN. BIS-LIN molecule includes two secondary amino groups capable to react, while BIS-TER molecule has just one primary group. BIS-TER provides weight yield of HEPIP based on the weight of reacted amine substantially higher than BIS-LIN over a wide range of conversion values as shown in Figure 1. The yields of TEDA of both the bis-derivatives are comparable. In the case of BIS-LIN the extent of reactions leading to macro-molecular compounds is significantly higher than in the case of BIS-TER, which may be followed in values of C index where for BIS-LIN values may be attained close to 0.5. It follows from mass balance of experiments that the amount of gaseous products was minimum in both the cases.
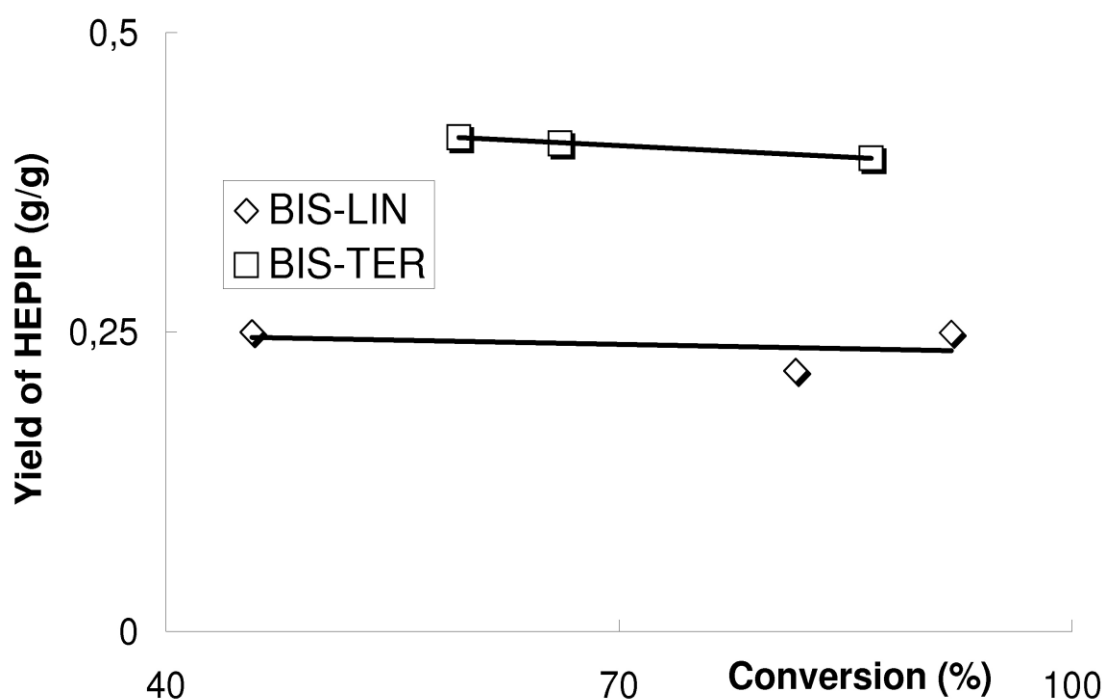

Fig. 1. Dependence of weight yield of HEPIP based on the weight of reacted initial compound for various values of conversion of BIS-LIN and BIS-TER, respectively.

Table 4. Weight concentration of the compounds in the reaction mixture for different conversion of BIS-TER. Concentration of BIS-TER in the feed water solution was 50 % wt.

WHSV [h⁻]	4.3	3.2	2.5
Conversion	59.4	66.1	86.7
PIP	0.16	0.22	0.42
EPYR	0.08	0.10	0.16
EPIP	0.09	0.12	0.23
TEDA	1.77	2.23	3.93
HEPIP	12.35	13.58	17.59
EHEPIP	0.51	0.61	1.00
BIS_TER	20.48	17.09	6.83
BHEPIP	1.05	1.10	0.96
BPIPE	0.09	0.13	0.22
C index	0.78	0.76	0.69

3.2. Piperazine and its hydroxyethyl derivatives

It was found that under conditions of experiments carried out in our study, that means temperature 350°C, molar ratio PIP : water = 1 : 12, and the range of catalyst load similar to previous experiments, PIP has low reactivity. Maximum PIP conversion attained was 15 % while merely two main products were detected that is TEDA and EPIP, see Table V. The PIP low reactivity is caused by thermodynamic stability of six-member ring. Reichle [12] came to the same conclusion in his paper. High values of the C index correspond to the low PIP conversions and no conclusion with regard to other experiments may not be made.

Table 5. Weight concentration of the compounds in the reaction mixture for different conversion of PIP. Concentration of PIP in the feed water solution was 28.4 % wt.

WHSV [h⁻]	6.8	4.3	1.5
Conversion	6.5	10.4	15.1
PIP	26.63	25.87	24.12
EPIP	0.01	0.02	0.07
TEDA	0.31	0.43	1.49
C index	0.95	0.91	0.91

Table 6. Weigh concentration of the compounds in the reaction mixture for different conversion of HEPIP. Concentration of HEPIP in the feed water solution was 46.7 % wt.

WHSV [h-]	4.3	2.8	2.2	1.5
Conversion	48.1	61.9	70.2	85.4
PIP	0.75	1.28	1.36	2.08
EPYR	0.10	0.21	0.31	0.46
EPIP	0.25	0.54	0.89	1.39
TEDA	7.09	11.96	13.50	18.22
HEPIP	24.29	17.98	14.13	7.31
EHEPIP	0.79	1.50	1.53	1.66
BHEPIP	0.07	0.09	0.05	0.05
BPIPE	0.48	0.91	1.05	1.06
EBPIPE	0.24	0.64	0.86	1.19
C index	0.75	0.79	0.76	0.73

HEPIP provides TEDA as the main product. Important by-products are PIP, EPIP, EHEPIP, BPIPE, and 1-(4-ethylpiperazine)-2-piperazineethane (EBPIPE). In this case the EPIP concentration is significantly higher than in the previous examples. It is obvious in this case that HEPIP is the precursor of the EPIP formation. This may be considered as the confirmation of our view that AEPIP is the precursor for the EPIP formation in the case EDA is used as raw material. When maximum conversion of 85 % was attained the selectivity to TEDA of 53 % was reached. The summary or results of the experiment with HEPIP is presented in Table 6. In terms of macro-molecular compound formation HEPIP is comparable to HEEDA.

BHEPIP, the last compound studied underwent mostly decomposition to HEPIP and cycling to TEDA over ZSM-5. Samples taken featured very strong aldehyde odour. BHEPIP either undergoes direct elimination of hydroxyethyl group and forms acetaldehyde, or water is released while forming N-hydroxyethyl-N'-vinylpiperazine (VHEPIP), which may be further hydrolysed to form HEPIP and acetaldehyde and this reaction may be reversible. Potential reaction pathways of the acetaldehyde formation are demonstrated in scheme 4. The weight yield of TEDA+HEPIP based on the reacted BHEPIP was relatively high (37 %) at conversion of 63 %. Appropriate summary can be found in Table 7. Values of the C index are comparable to the values obtained in the case of BIS-TER.
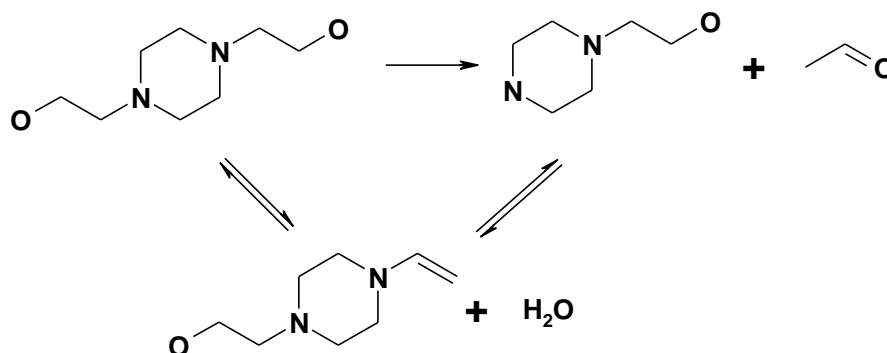
Scheme 4. Formation of N-hydroxyethyl-N'-vinylpiperazine

Table 7. Weigh concentration of the compounds in the reaction mixture for different conversion of BHEPIP. Concentration of BHEPIP in the feed water solution was 54 % wt.

WHSV [h-]	5.2	3.4	1.8
Conversion	34.5	40.4	63.2
PIP	0.05	0.08	0.14
EPYR	0.02	0.04	0.13
EPIP	0.06	0.10	0.20
TEDA	2.66	4.34	7.77
HEPIP	2.45	3.48	4.86
EHEPIP	0.35	0.59	1.41
VHEPIP	0.25	0.54	1.15
BHEPIP	35.76	32.77	20.09
C index	0.77	0.78	0.68

4. Conclusion

It was found that monoethoxylates of EDA and PIP provide significantly higher weight yield than any of the bisethoxylates investigated. The use of monoethoxylates for the TEDA synthesis did not give as high yield as in the case just EDA was used, although the process may be economically more advantageous because a portion of ethylenediamine is substituted by substantially cheaper ethylene oxide.

Symbols used

TEDA	1,4-diazabicyclo[2,2,2]octane
EDA	ethylenediamine
PIP	piperazine
AE	2-aminoethanol
ETOX	ethylene oxide
HEEDA	N-(2-hydroxyethyl)-ethylenediamine
HEPIP	N-(2-hydroxyethyl)piperazine
BIS-LIN	N,N'-bis(2-hydroxyethyl)ethylenediamine
BIS-TER	N,N-bis(2-hydroxyethyl)ethylenediamine
BHEPIP	N,N'-bis(2-hydroxyethyl)piperazine
DETA	diethylenetriamine
AEPIP	N-aminoethylpiperazine
EPIP	N-ethylpiperazine
PYR	pyrazines

EPYR   ethylpyrazine
DMPYR   2,3-dimethylpyrazine
HEAEPIP   N-hydroxyethyl-N`-aminoethylpiperazine
BPIPE   1,2-bispiperazinoethane
EHEPIP   N-hydroxyethyl-N'-ethylpiperazine
EBPIPE   1-(4-ethylpiperazine)-2-piperazineethane
VHEPIP   N-hydroxyethyl-N'-vinylpiperazine

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