

## PREDICTING THE DISTRIBUTION OF ETHOXYLATION HOMOLOGUES WITH A PROCESS SIMULATOR

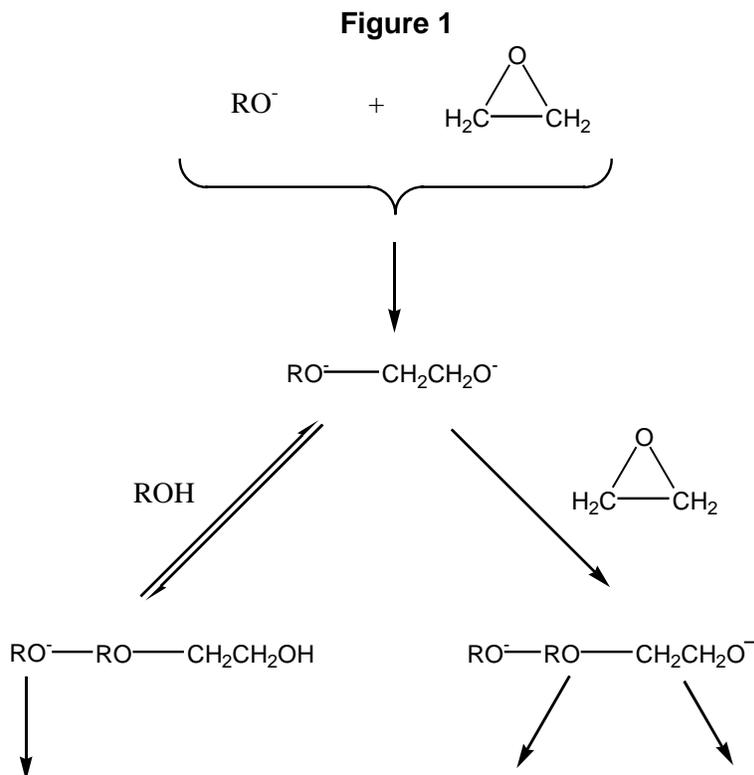
Nathan Massey, Chemstations, Inc.

### Introduction

Ethoxylates are generally obtained by additions of ethylene oxide (EO) to compounds containing dissociated protons. Substrates used for ethoxylation are primarily linear and branched C<sub>12</sub>-C<sub>18</sub> alcohols, alkyl phenols, nonyl (propylene trimer) or decyl (propylene tetramer) groups, fatty acids and fatty acid derivatives. The addition of EO to a substrate containing acidic hydrogen is catalyzed by bases or Lewis acids. Amphoteric catalysts, as well as heterogeneous catalysts are also used. The degree of ethoxylation ( the moles of EO added per mole of substrate ) varies over wide ranges, in general between 3 and 40, and is chosen according to the intended use. As an illustration of how this distribution might be predicted using a process simulator, Chemcad was used to simulate the ethoxylation of Nonylphenols.

### Description of the Ethoxylation Chemistry

The reaction mechanisms of base catalyzed and acid catalyzed ethoxylation differ, which affects the composition of the reaction products. In base catalyzed ethoxylation an alcoholate anion, formed initially by reaction with the catalyst ( alkali metal, alkali metal oxide, carbonate, hydroxide, or alkoxide ) nucleophilically attacks EO. The resulting union of the EO addition product can undergo an equilibrium reaction with the alcohol starting material or ethoxylated product, or can react further with EO:



As Figure 1 illustrates, in alkaline catalyzed ethoxylations several reactions proceed in parallel. The addition of EO to an anion with the formation of an ether bond is irreversible.

Proton exchange, occurring as an electrolyte reaction, is fast. The addition reaction of EO to an existing anion is the rate determining step. Thus in a reaction mixture, the more acidic species preferentially react with EO. If carboxylic acids or phenols are ethoxylated, the reaction proceeds exclusively via the left hand path of Figure 1, and the initially formed monoethylene glycol ester or ether only reacts further when all the starting material in the reaction mixture is consumed.

The fast equilibrium proton exchange reaction which precedes the addition of EO to the anionic species leads to a peculiarity of the reaction rate in the case of strongly acidic substrates such as carboxylic acids or phenols. Due to the lower nucleophilicity of their conjugate bases, these bases react relatively slowly until the starting material is consumed. Thereafter the reaction rate increases sharply with further supply of EO since the ethoxylate anions now present react significantly faster with EO than do the anions of the carboxylic acids or phenols.

The situation is reversed for the ethoxylation of alcohols, but that discussion is beyond the scope of this paper.

When Lewis acids are used as catalysts, homologue distributions approximating the Poisson distribution are obtained because in this case it is not the proton activity but the nucleophilicity of the substrate that determines the reaction pathway. Lewis acids activate EO and not the alcohol.

Lewis acids are not frequently used as catalysts since their removal from the reaction product is tedious and because they lead to the formation of undesirable side products.

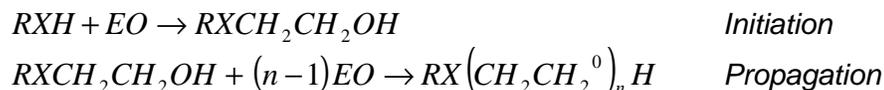
### **Process Description**

Industrial ethoxylations are carried out mainly in a batchwise manner. The substrate together with the catalyst is first placed in the reaction vessel. The water introduced with the catalyst and the water formed in the first reaction is removed by heating or by passing N<sub>2</sub> gas through the reaction mixture to avoid formation of polyglycols. The catalyst content is usually 0.1-1.0%. The ethoxylation is carried out between 130-180°C. The reactor contents must be cooled during the addition of EO. The reaction is carried out at 1-6 atm. The liquefied EO is dosed into the reaction.

### **The Chemcad Model**

The kinetics of nonylphenol ethoxylations, catalyzed by KOH was studied by Santacesaria, et al, at different temperatures, catalyst concentrations, and ethylene oxide pressures. Based on the kinetic parameters provided by this work, a semi-batch kinetic reactor flowsheet was developed in Chemcad based upon the assumption that the EO ring opening is the rate determining step. The work of Santacesaria, et al, is summarized below.

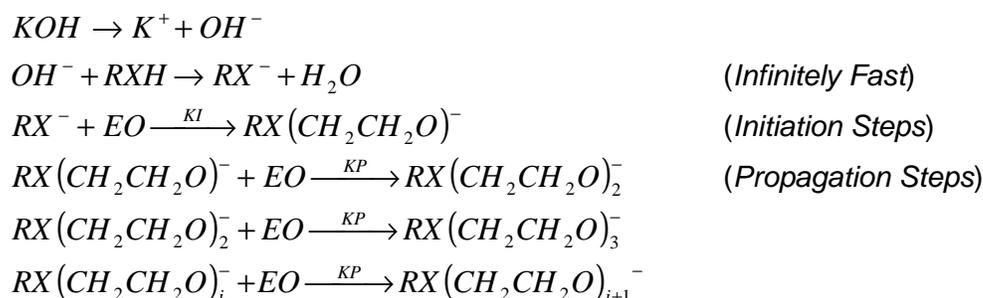
1. A simplified reaction scheme for the polyethoxylation of nonylphenol can conveniently be expressed like so;



No termination step exists.

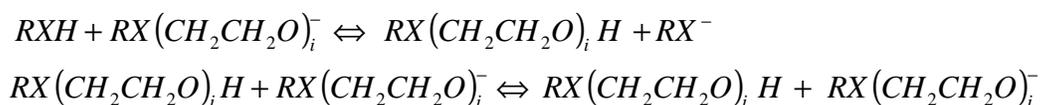
Under base catalyzed conditions, reaction water and product distributions are influenced by the relative rates of the above steps and the relative acidity of  $RXH$  and  $RX(CH_2CH_2O)_nH$ .

2. A more detailed mechanism using  $KOH$  as the catalyst would be;



Note: That in this model the catalyst,  $KOH$ , participates directly in the reaction scheme.

3. It is reasonable to assume that the ring opening of  $RO$  is the rate determining step and that all the propagation steps are identical from the point of view of kinetics because of the similarity of the structure and the basicity of the polyethoxylated anions.
4. Together with the above reactions, the following proton exchange reactions must also be considered in the system:



Since the acidity does not change with chain length, that is,  $K_{e1} = K_{e2} = \dots = K_{en}$ , a unique equilibrium constant,  $K_e$ , can be considered. As a consequence,  $K_{eij}$ , can be assumed to be equal to one, thus the proton exchange reaction does not affect the polymerization rate.

5. For solving the proposed kinetic model, it is necessary to know the solubility of  $EO$  in the evolving reaction mixture. Solubility measurements were performed for  $EO$  in nonylphenol and in polyethoxylated mixture. From the reported data, it is possible to observe that  $EO$  has about the same solubility in both solutions and that it follows Henry's law. It is therefore possible to assume that the  $EO$  solubility is constant during the reaction at a fixed temperature.

6. In the temperature range 70-130°C the chemical regime is operative and reaction rates not strongly affected by stirring speed. At higher temperatures the physical regime is controlling and reaction rates are strongly affected by stirring speeds.

Using these assumptions, the Chemcad model was built as summarized below.

The model was first run as Santacesaria (et al) ran their experiments. The results were then compared with the reported data. Figures 2 and 3 summarize this comparison.

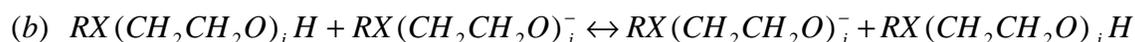
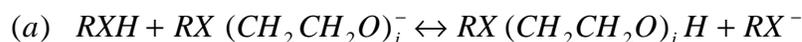
### Key Aspects of the Chemcad Model

- 1) The catalyst disassociation reaction,  $\text{KOH} \rightarrow \text{K}^+ + \text{OH}^-$ , is assumed to be infinitely fast, irreversible and complete.
- 2) The proton donor reaction,  $\text{RXH} + \text{OH}^- \rightarrow \text{RX}^- + \text{H}_2\text{O}$  is also taken to be infinitely fast, irreversible, and complete.
- 3) The initiation step,  $\text{RX}^- + \text{EO} \xrightarrow{k_1} \text{RX}(\text{CH}_2\text{CH}_2\text{O})^-$  is modeled as an irreversible, kinetic (rate limited) reaction.
- 4) The propagation step(s),



are modeled as irreversible, kinetic (rate limited) reactions. The rate constant,  $k_p$ , is taken to be the same for each propagation step  $i$ . This is acceptable due to the similarity of the structure and the basicity of the poly ethoxylated anion homologues. The propagation steps are explicitly modeled through  $i + 1 = 10$ . For the purpose of this simulation this was considered to be adequate.

- 5) The proton exchange reactions,



are modeled as fast equilibrium reactions. For reaction (a) the equilibrium constant,  $K_{e_i}$ , taken to be the same for all values of  $i$  so that,

$$K_{e_1} = K_{e_2} = \dots = K_{e_i}$$

This is justified by Santacesaria on the basis that;

- (i) the equilibrium is primarily a function of the acidity of the polyethoxylated homologue;
- (ii) the acidity of these homologues does not vary with chain length.

The values of  $K_{e_i}$  used in this simulation varies with the catalyst employed. A value of 4.73 was calculated for this system (see Santacesaria, et.al.). This reaction was explicitly modeled for all  $i$  up to 10.

For reaction (b) the equilibrium constant,  $K_{e_{ij}}$ , is equal for all values of  $i$  and  $j$  (see Santacesaria, et.al.). It therefore must be equal to one. As a result, this reaction does not affect the ethoxylation rate or the ethoxylation homologue distribution. Therefore, all reactions of type 5(b) were omitted from the simulation.

- 6) The EO equilibrium data was fit to the Henry's Gas Law equation and this relation was used to compute the K-Values for EO. All other K-Values were calculated using the NRTL equation.
- 7) The process is modeled as a semi batch system with EO being fed. The following information is relevant :
- i) the catalyst and the substrate are initially placed in the reaction vessel at ambient temperature (25°C).
  - ii) The reaction mass design temperature is isothermal at 73°C. The batch reaction time is to be 8 hours. For this period of time EO is to be added and the controller set points are to be 73°C (for the reaction mass temperature). After this the reaction mass is to be cooled to 35°C. Therefore, at 4 hours the set point is changed to 35°C.

The complete model is summarized in Tables 1-3.

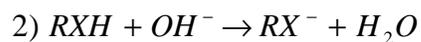
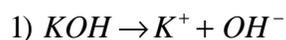
**Table 1**  
**Kinetics Reactions Summary**

	Reaction	Rate Expression	Type
1)	$RX^- + EO \rightarrow RX(EO)^-$	$r_1 = k_1 [RX^-][EO]$	Initiation
2)	$RX(EO)^- + EO \rightarrow RX(EO)_2^-$	$r_2 = k_p [RX(EO)^-][EO]$	Propagation
3)	$RX(EO)_2^- + EO \rightarrow RX(EO)_3^-$	$r_2 = k_p [RX(EO)_2^-][EO]$	Propagation
4)	$RX(EO)_3^- + EO \rightarrow RX(EO)_4^-$	$r_2 = k_p [RX(EO)_3^-][EO]$	Propagation
5)	$RX(EO)_4^- + EO \rightarrow RX(EO)_5^-$	$r_2 = k_p [RX(EO)_4^-][EO]$	Propagation
6)	$RX(EO)_5^- + EO \rightarrow RX(EO)_6^-$	$r_2 = k_p [RX(EO)_5^-][EO]$	Propagation
7)	$RX(EO)_6^- + EO \rightarrow RX(EO)_7^-$	$r_2 = k_p [RX(EO)_6^-][EO]$	Propagation
8)	$RX(EO)_7^- + EO \rightarrow RX(EO)_8^-$	$r_2 = k_p [RX(EO)_7^-][EO]$	Propagation
9)	$RX(EO)_8^- + EO \rightarrow RX(EO)_9^-$	$r_2 = k_p [RX(EO)_8^-][EO]$	Propagation
10)	$RX(EO)_9^- + EO \rightarrow RX(EO)_{10}^-$	$r_2 = k_p [RX(EO)_9^-][EO]$	Propagation

**Table 2**  
**Equilibrium Reactions Summary**

	Reaction	Equilibrium Expression	Type
1)	$RXH + RX(EO)_1^- = RX^- + RX(EO)H$	$Ke = \frac{[RX^-][RX(EO)H]}{[RXH][RX(EO)_1^-]}$	Proton Exchange
2)	$RXH + RX(EO)_2^- = RX^- + RX(EO)_2H$	$Ke = \frac{[RX^-][RX(EO)_2H]}{[RXH][RX(EO)_2^-]}$	Proton Exchange
3)	$RXH + RX(EO)_3^- = RX^- + RX(EO)_3H$	$Ke = \frac{[RX^-][RX(EO)_3H]}{[RXH][RX(EO)_3^-]}$	Proton Exchange
4)	$RXH + RX(EO)_4^- = RX^- + RX(EO)_4H$	$Ke = \frac{[RX^-][RX(EO)_4H]}{[RXH][RX(EO)_4^-]}$	Proton Exchange
5)	$RXH + RX(EO)_5^- = RX^- + RX(EO)_5H$	$Ke = \frac{[RX^-][RX(EO)_5H]}{[RXH][RX(EO)_5^-]}$	Proton Exchange
6)	$RXH + RX(EO)_6^- = RX^- + RX(EO)_6H$	$Ke = \frac{[RX^-][RX(EO)_6H]}{[RXH][RX(EO)_6^-]}$	Proton Exchange
7)	$RXH + RX(EO)_7^- = RX^- + RX(EO)_7H$	$Ke = \frac{[RX^-][RX(EO)_7H]}{[RXH][RX(EO)_7^-]}$	Proton Exchange
8)	$RXH + RX(EO)_8^- = RX^- + RX(EO)_8H$	$Ke = \frac{[RX^-][RX(EO)_8H]}{[RXH][RX(EO)_8^-]}$	Proton Exchange
9)	$RXH + RX(EO)_9^- = RX^- + RX(EO)_9H$	$Ke = \frac{[RX^-][RX(EO)_9H]}{[RXH][RX(EO)_9^-]}$	Proton Exchange
10)	$RXH + RX(EO)_{10}^- = RX^- + RX(EO)_{10}H$	$Ke = \frac{[RX^-][RX(EO)_{10}H]}{[RXH][RX(EO)_{10}^-]}$	Proton Exchange

**Table 3**  
**Stoichiometric Reactions**



**Table 4**  
**Solubility Equilibrium Data Collected For Ethylene Oxide in Nonylphenol and Nonylphenol Poly(ethylene oxide)<sup>a</sup>**

Solvent	Added Volume of EO	P <sub>EO</sub> , atm	K, atm	T, °C
Nonylphenol	15.58	2.00	11.2	100
	20.70	2.50	10.7	100
	23.10	2.95	11.2	100
	25.50	3.10	11.4	100
	28.62	3.40	11.3	100
	11.32	2.20	19.0	125
	12.45	2.35	18.8	125
	14.50	2.72	18.4	125
	15.77	2.90	18.4	125
	Nonylphenol Poly (ethylene oxide)	1.25	2.10	12.3
13.75		2.45	11.3	100
15.25		2.68	11.3	100
16.50		2.92	10.8	100
18.00		3.05	10.9	100
10.30		2.80	23.5	125
11.55		3.15	24.1	125
12.76		3.40	22.6	125

<sup>a</sup> Average molecular weight, 629. Void reactor volume was 800 cm<sup>3</sup>, while the volume of the solvent was 172 cm<sup>3</sup>.

### Results:

Using the above model, Chemcad runs were made at 73°C, 3 atm., and 53.4 moles of Nonylphenol per mole of catalyst. This temperature and pressure was chosen because at their conditions the chemical regime is operative and the reaction rates are not significantly affected by stirring rates. Figure 2 shows the experimental and calculated moles of EO reacted per mole of initial nonylephenol as a function of time. Experimental and calculated oligomer distributions are reported in Figure 3.

Figure 2

Ethoxylation of Nonylphenol at 73C  
Moles of EO reacted/moles of NP reacted

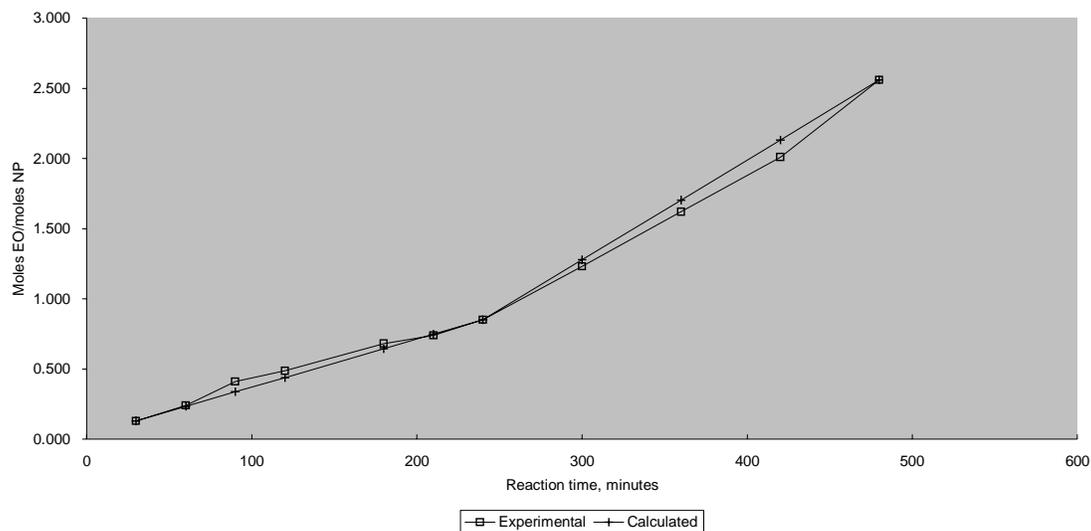
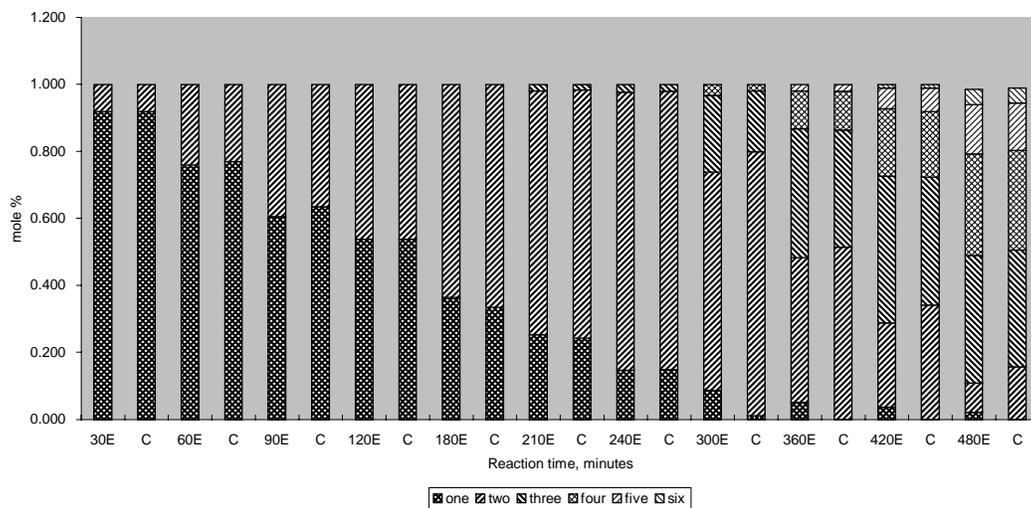


Figure 3

Ethoxylation of Nonylphenol at 73C  
Homologue Distribution



## References

1. Santacesaria, E., Serio, M., and Lisi, L.; "Kinetics of Nonylphenol Polyethoxylation Catalyzed by Potassium Hydroxide"; Ind. Eng. Chem. Res.; 1990; 29; 719-725.
2. Hreczueh, W., Miskiewicz, W., Szymanowski, J., Zimoch, J., and Jerzykiewicz, A.; "High Ethoxylated Alcohols with Narrow Distribution of Homologues"; J. Chem. Biotechnol. ; 1996; 67; 53-60.
3. Santacesaria, E., Serio, M., Garaffa, R., and Addino, G.; "Kinetics and Mechanisms of Fatty Alcohol Polyethoxylation"; Ind. Eng. Chem. Res.; 1992; 31; 2413-2421.
4. Serio, M., Tesser, R., Felippone, F., and Santacesaria, E.; "Ethylene Oxide Solubility and Ethoxylation Kinetics in the Synthesis of Nonionic Surfactants"; Ind. Eng. Chem. Res.; 1995; 34; 4092-4098.