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Kinetics of Ethoxylation and Propoxylation of Ethylene Glycol Catalyzed by KOH

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In the present paper the kinetics of ethoxylation and of propoxylation of ethylene glycol catalyzed by KOH have been studied. The ethoxylation of ethylene glycol occurs with a rate that initially is higher than that observed for a fatty primary alcohol, while the propagation rate is practically the same. A kinetic model based on the reaction mechanisms similar to the one developed for fatty alcohols has been used for interpreting ethoxylation kinetic runs and the corresponding kinetic parameters have been determined. The propoxylation reaction occurs following a more complicated reaction scheme considering that the reaction of a primary hydroxyl gives place preferentially to a secondary one and this last is less reactive. A kinetic model has been developed for taking into account this peculiar behavior and the corresponding kinetic parameters have been determined. Independent experimental runs have been performed to evaluate densities of any possible reaction mixture and the corresponding ethylene and propylene oxide solubilities.

Introduction

Ethoxylation and propoxylation are extensively used by industry to produce a large number of products. An important class of such products are poly(ethylene glycol)s, polypropylene glycols, and ethylene oxide–propylene oxide copolymers that are largely used as chemical intermediates, lubricants, industrial surfactants, and components for cosmetic and personal care formulations.¹

Different classes of catalysts operating with different mechanisms influencing reaction rate and oligomers distribution can promote the reactions of ethoxylation and propoxylation.² It is possible to induce, for example, polymerization in the presence of an acid catalyst of both Brönsted³ and Lewis type.⁴ It is also possible to favor the reaction by using transition metals complexes.^{5–8} Some heterogeneous catalysts have also been proposed.^{9–12}

Despite the large number of papers and patents published in the literature dealing with the different mentioned catalysts and the possibility of obtaining peaked oligomers distribution, the syntheses of poly(ethylene glycol)s, polypropylene glycols, and ethylene oxide–propylene oxide copolymers are still performed in industry in the presence of alkaline catalysts such as KOH and NaOH.

Very few papers have been published on the kinetics of these reactions promoted by alkaline catalysts.^{13–15} The reactivity of ethylene oxide and propylene oxide with, respectively, primary and secondary hydroxyls, in the presence of the most used KOH catalyst, has been studied by Di Serio et al.¹⁶ in a previous paper. The authors obtained the values of the kinetic constants for the addition of respectively ethylene and propylene oxide to 1- and 2-octanol. In that work it was suggested that the obtained kinetic constants could be useful for simulating ethylene–propylene oxide copolymerization, the addition of ethylene oxide to a propoxylated chain, and the addition of propylene oxide to an ethoxylated chain provided that the solubilities of the epoxides in

the reaction mixtures are known as well as the densities of these mixtures.

In this paper we have studied the ethoxylation and the propoxylation of ethylene glycol to provide more detailed data on these reactions.

Kinetic data have been obtained both by measuring epoxide consumption and by analyzing some samples withdrawn at different reaction times.

The evolution with time of the epoxide consumption and of the oligomer distributions have been interpreted by using a detailed kinetic model. Solubilities and reaction mixture densities, necessary for the elaboration of kinetic data, have been measured with dedicated experiments whose results have been interpreted by using both empirical and theoretical approaches. The kinetic parameters of the two systems studied have been determined by mathematical regression analysis of the experimental data. The values of the kinetic parameters obtained have been compared with those reported in previous papers.^{17,16}

Experimental Section

Kinetic Runs. Kinetic runs have been performed in a reactor well described elsewhere.¹⁷ The control of pressure, temperature, and epoxide fed to the reactor was fully automated by a computer. Ethylene oxide and propylene oxide were furnished respectively by SIAD and Fluka. Epoxide consumption was directly measured and recorded at each instant with a balance measuring the weight loss of the epoxide bottle. The epoxide in the bottle was pressurized with nitrogen at about 10 bar and automatically fed to a reactor to keep the preset pressure value (2 bar) constant. A weighed amount of KOH was used as the catalyst. Samples of the reaction mixtures were withdrawn at different times and analyzed.

The runs were made using respectively ethylene glycol (EG) and tetraethylene glycol (TEG) as starters. Ethylene glycol and tetraethylene glycol were both supplied by Fluka. The list of the performed kinetic runs together with the used operative conditions applied are reported in Tables 1 and 2.

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Table 1. List of the Kinetic Ethoxylation Runs Performed

run	substrate	substrate amount (g)	epoxide (2 bar)	<i>T</i> (K)	KOH (g)	<i>k</i> ₀ (cm ³ /(mol min))	<i>k</i> _p (cm ³ /(mol min))	<i>K</i> _e
A1	EG	241.0	EO	353	1.50	910	217	4.4
A2	EG	242.3	EO	375	1.51	2964	919	3.2
A3	EG	245.0	EO	405	1.52	8312	18447	3.0
A4	TEG	249.3	EO	356	1.55		259	
A5	TEG	284.4	EO	373	1.72		713	
A6	TEG	252.0	EO	394	1.57		2828	

Table 2. List of the Kinetic Propoxylation Runs Performed

run	substrate	substrate amount (g)	epoxide (2 bar)	<i>T</i> (K)	KOH (g)	<i>k</i> _{pp} (cm ³ /(mol min))	<i>k</i> _{ps} (cm ³ /(mol min))	<i>K</i> _{e1}	<i>K</i> _{e2}
B1	EG	249.8	PO	378	1.46	334		0.6	
B2	EG	261.6	PO	393	1.53	1090	293	0.7	0.3
B3	EG	251.5	PO	413	1.47	3222	453	0.8	0.2

Table 3. Response Factor Used in the Analysis

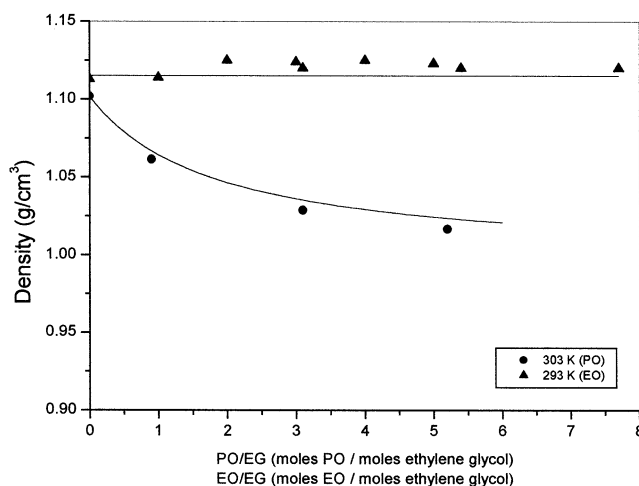
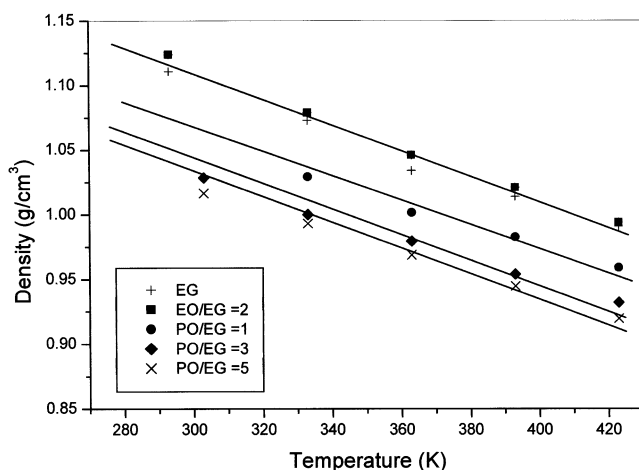
HPLC analysis—RI detector		GC analysis—FID detector	
species	molar response factor	species	weight response factor
EG	1	EG	1
EG + 1EO	0.459	EG + <i>n</i> PO,	0.725
EG + <i>n</i> EO,	0.286	<i>n</i> = 1, ...	
<i>n</i> = 2, ...			

Samples Analysis. The samples obtained from ethoxylation reactions were analyzed by the HPLC technique while the ones obtained from propoxylation reactions were analyzed by the GC technique.

A Diolic bonded phase Lichrosphere 100–5- μ m column supplied by Merck and a Jasco Refractive Index detector 830–RI at 308 K were used for the HPLC analysis. The feed rate of the solvent was kept at 0.8 cm³/min using a Jasco Pump 880-PU. With the solvent mixture *n*-hexane:2-propanol:water:acetic acid = 200:80:50:1, all the oligomers of the mixture are well resolved except the ethylene glycol and the monoadduct that have similar retention times. To resolve these two compounds, it is necessary to use a different solvent composition, that is, *n*-hexane:2-propanol:water:acetic acid = 110:100:10:1. In the latter solvent mixture the solubility of higher adducts is poor, so to have complete distribution, two analyses with the two different solvents mixtures were performed on the same sample.

The molar response factors were determined using pure samples of different oligomers (ethylene glycol, monoethylene glycol, diethylene glycol, triethylene glycol, and tetraethylene glycol) supplied by Fluka. The values obtained are reported in Table 3. The molar response factors were tested by comparing the value of the ethylene oxide consumption obtained by mass balance applied to the oligomer distribution determined by HPLC analysis and the value measured by weight loss of the ethylene oxide bottle observed during the kinetic runs. The differences in the two values was <3%.

A 25 m \times 0.32 mm i.d. HP1 column (dimethylpolysiloxane gum) was used for GC analysis taking the oven temperature at 343 K for 1.5 min and then heating at a rate of 20 K/min up to 553 K. A FID detector kept at 573 K was used. The mass oligomers response factors have been calculated by assuming that the FID response would be proportional to the mass of each species by a constant factor. This factor was determined by regression analysis on several experimental data of propylene oxide consumption determined by weight at the end of each run. The differences between calculated and experimental PO consumption determined through the obtained response factors are <3%.

**Figure 1.** Dependence of density from the mean adducts number in the chains (dots are experimental data; lines are calculated).**Figure 2.** Dependence of density from the temperature for species with different adducts number in the chains (dots are experimental data; lines are calculated).

Density Measurements. To evaluate reaction volume and concentrations correctly, it is necessary to know the density of the reaction mixture at any reaction time. For this purpose, the density of the ethylene glycol and of the corresponding ethoxylated and propoxylated products, with an average number of alkylene oxide groups ranging between 0 and 8, were measured with a pycnometer, at different temperatures.

The obtained data are reported in Figures 1 and 2. As can be seen, the density is quite constant for the ethoxylated products while it decreases with the mean

Table 4. Relationships Giving Density as a Function of Both Temperature and Mean Number of Propylene Oxide Adducts per Mole of Starter (EG) [Densities of All Ethylene Oxide Adducts Are the Same as Those of EG ($n_{PO} = 0$)]^a

A	B	C	D	E
1.398	-9.672×10^{-4}	-0.1055	5.266	9.524

$$^a d = A + BT + [CDn_{PO}/(E + Dn_{PO})].$$

number of propoxide groups in the chain. The temperature affects the density in a similar way for ethylene glycol and ethoxylated and propoxylated products.

A single relation for determining the density as a function of the number of EO and PO adducts and temperatures was derived by processing all the obtained experimental data. This relation is reported in Table 4 together with the numerical values of the parameters. The agreements between experimental and calculated data by using the relation of Table 4 can be appreciated in Figures 1 and 2.

Determination of Alkylene Oxides Solubility.

Alkylene oxides solubility runs were performed in the same reactor employed for kinetic runs by introducing a weighed amount of the organic substrate, that is, ethylene glycol or its ethoxylated/propoxylated derivatives. The ethoxylated/propoxylated derivatives, normally obtained as reaction products, were treated several times with ion-exchange resin of Amberlite IRC 76, that is, resins with moderate acidity, to eliminate any trace of potassium catalyst. Weighed amounts of alkylene oxide were then added at a prefixed temperature, and the equilibrium pressure was measured by a pressure transducer.

The obtained results are reported in Figures 3 and 4.

The solubility data have been described by using the Wilson model for calculating liquid activity coefficients, while the vapor phase was considered ideal in calculation, as previously suggested by Di Serio et al.:¹⁸

$$x_{AO} = P_{AO}/(\gamma_{AO}P_{AO}^0) \quad (1)$$

The vapor pressures of ethylene oxide and propylene oxide were determined by using the following Antoine equation:¹⁹

$$P_{EO}^0 = \exp[16.74 - 2568/(T - 29.01)]/760 \quad (2)$$

$$P_{PO}^0 = \exp[15.32 - 2108/(T - 64.87)]/760 \quad (3)$$

with P^0 in bar and T in K.

The Wilson equations for calculating the activity coefficients are the following:

$$\ln \gamma_1 = -\ln(x_1 + x_2\Lambda_{12}) + x_2[\Lambda_{12}/(x_1 + x_2\Lambda_{12}) - \Lambda_{21}/(x_1\Lambda_{21} + x_2)] \quad (4)$$

$$\ln \gamma_2 = -\ln(x_1\Lambda_{21} + x_2) - x_1[\Lambda_{12}/(x_1 + x_2\Lambda_{12}) - \Lambda_{21}/(x_1\Lambda_{21} + x_2)] \quad (5)$$

The two interaction parameters Λ_{12} and Λ_{21} were considered dependent on the mean number of alkylene oxide adducts according to the following relations:

$$\Lambda_{12} = A_{12} + B_{12}n_{AO} + C_{12}n_{AO}^2 \quad (6)$$

$$\Lambda_{21} = A_{21} + B_{21}n_{AO} + C_{21}n_{AO}^2 \quad (7)$$

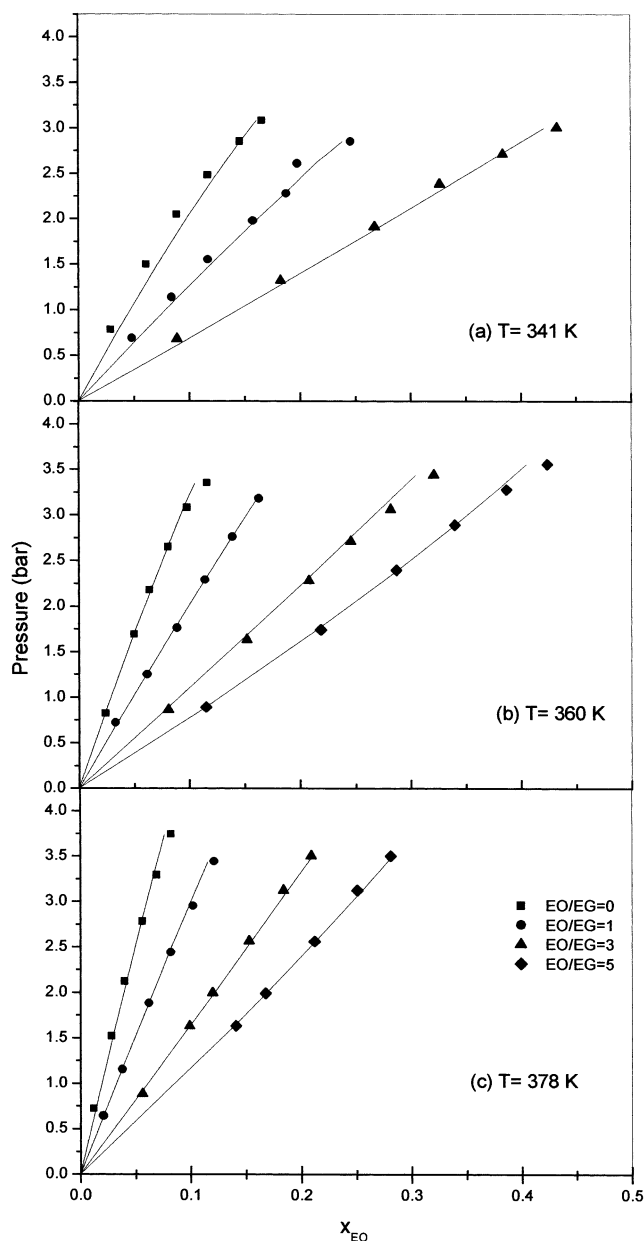


Figure 3. Ethylene oxide solubility in different substrates for different temperatures (dots are experimental data; lines are calculated).

The dependence of these parameters on temperature has been found to be negligible.

The parameters of the model, that is, A_{12} , A_{21} , B_{12} , B_{21} , C_{12} , and C_{21} , were determined through regression analysis on the experimental data²⁰ and are reported in Table 5. The agreement obtained is satisfactory, as can be seen in Figures 3 and 4.

From the alkylene oxide molar fraction in the liquid the corresponding liquid concentration can be calculated:

$$[AO] = \frac{x_{AO}}{(1 - x_{AO})} \frac{S}{V_1} \quad (8)$$

The liquid volume V_1 is then calculated using the following equation,

$$V_1 = S \left[\frac{x_{AO}}{1 - x_{AO}} \frac{M_{AO}}{d_{AO}} + \frac{M}{d} \right] \quad (9)$$

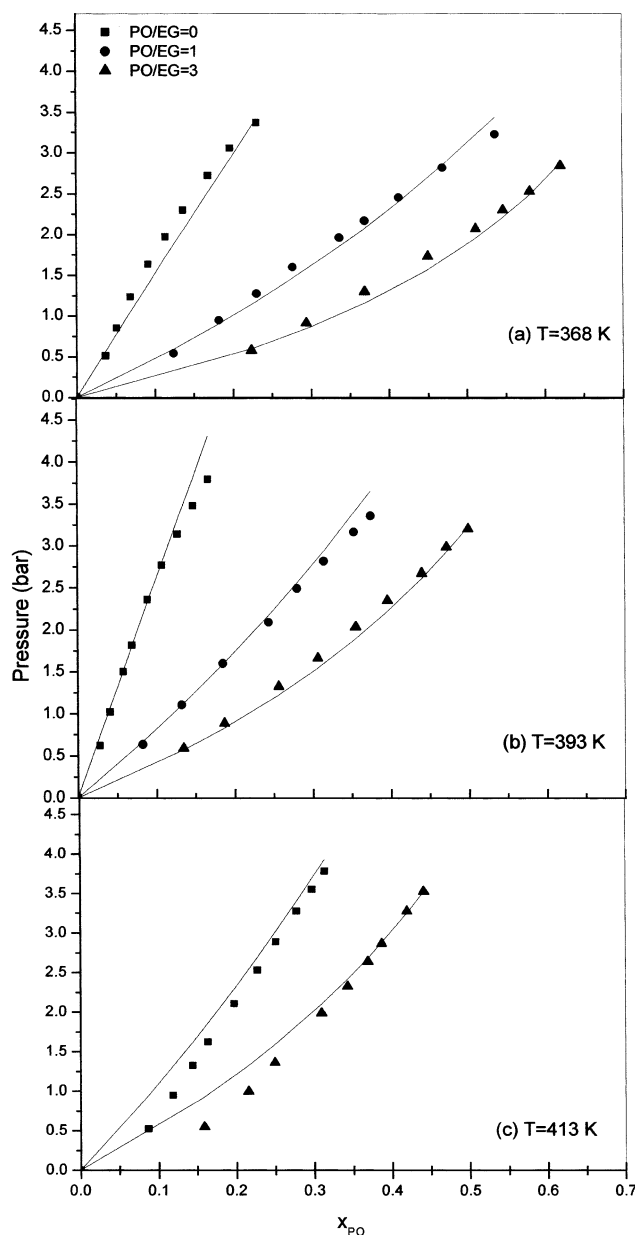


Figure 4. Propylene oxide solubility in different substrates for different temperatures (dots are experimental data; lines are calculated).

Table 5. Wilson Equation Parameters Obtained

alkoxide	A_{12}	B_{12}	C_{12}	A_{21}	B_{21}	C_{21}	n_{\max}
EO	1.0100	0.5290	-0.0244	-0.2460	0.1370	-0.00899	5
PO	1.5203	0.9163	0.275	-0.3476	0.1476	-0.02770	4

where x_{AO} is calculated using eq 1, while d is obtained by the equation and parameters reported in Table 4. Liquid alkylene oxide density (d_{AO}) is obtained by the Yeen and Woods equation,²¹ and the mean molecular weight of the ethoxylated products (M) is given by the equation

$$M = \left(\frac{AO}{S}\right)M_{AO} + M_S \quad (10)$$

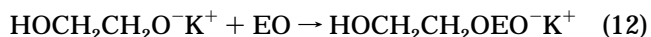
Results and Discussion

Ethoxylation Reaction. The mechanism of alcohol ethoxylation catalyzed by a metal hydroxide can be summarized as follows:²

(a) Catalyst Formation. The catalyst is formed in situ by the reaction of KOH with ethylene glycol, forming an ion pair:



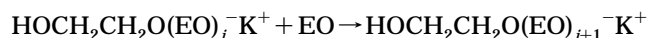
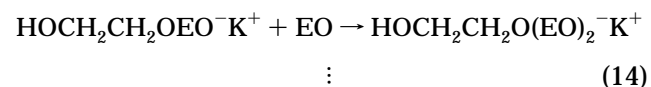
(b) Initiation. The glycolate anion reacts with ethylene oxide:



The occurring reaction can be classified as a nucleophilic substitution S_N2 . Consequently, the kinetic law for this reaction would be

$$r_0 = k_0[\text{HOCH}_2\text{CH}_2\text{O}^-\text{K}^+][\text{EO}] \quad (13)$$

(c) Propagations. The oxyethylene anions formed may be involved in successive propagation steps, such as

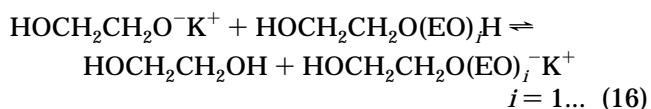


These reactions are also nucleophilic substitutions S_N2 and the corresponding kinetic laws are

$$r_1 = k_1[\text{HOCH}_2\text{CH}_2\text{OEO}^-\text{K}^+][\text{EO}] \quad (15)$$

$$r_i = k_i[\text{HOCH}_2\text{CH}_2\text{O}(\text{EO})_i^-\text{K}^+][\text{EO}]$$

(d) Proton Transfer. The oxyethylene anions are also involved in the following proton-transfer reactions:



The proton-transfer equilibrium constants are

$$K_{0i} = \frac{[\text{HOCH}_2\text{CH}_2\text{OH}][\text{HOCH}_2\text{CH}_2\text{O}(\text{EO})_i^-\text{K}^+]}{[\text{HOCH}_2\text{CH}_2\text{O}^-\text{K}^+][\text{HOCH}_2\text{CH}_2\text{O}(\text{EO})_i\text{H}]} \quad i = 1 \dots (17)$$

and depend on the relative acidity of both the substrate and the growing chain and on the relative stability of the corresponding ionic couples.

Ethylene oxide consumption, as a function of time, for the runs A1–A3 of Table 1 (ethylene glycol ethoxylation) is shown in Figure 5. As can be seen, the rate of reaction decreases with time. This behavior is due to the rate of the reaction of ethylene glycol with EO that is higher than the one of the corresponding formed adducts ($k_0 > k_1, \dots, k_i, \dots$).

The reactivity of the corresponding formed adducts can be considered independent of the length of the ethoxylated chain, as can be seen in Figure 6, where the ethylene oxide consumption rate is roughly constant during time for runs A4–A6 of Table 1 (tetraethylene glycol ethoxylation). This agrees with the results obtained in the ethoxylation of other primary alcohols.^{17,16}

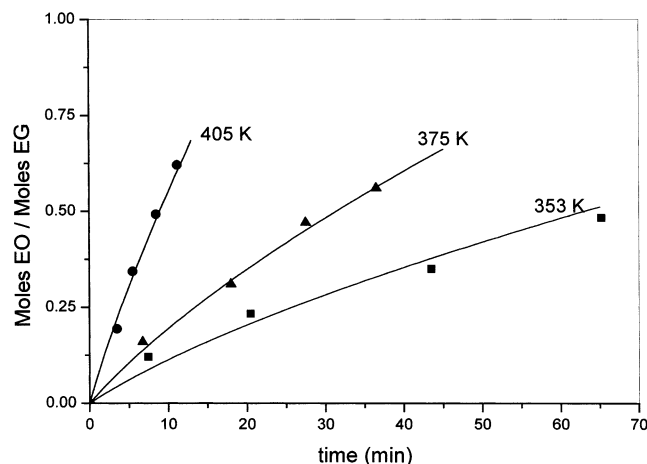


Figure 5. Ethylene oxide consumption related to moles of the starter in the ethoxylation of ethylene glycol (EG) performed at different temperatures (runs A1, A2, and A3 of Table 1). Dots are experimental; lines are calculated.

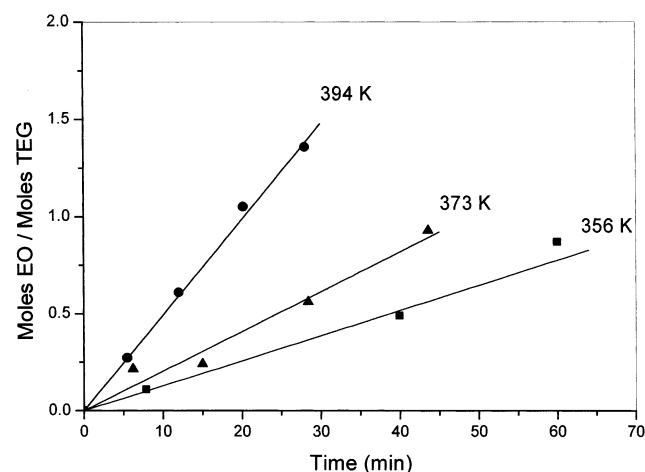


Figure 6. Ethylene oxide consumption related to the moles of the starter in the ethoxylation of tetraethylene glycol (TEG) performed at different temperatures (runs A4, A5, and A6 of Table 1). Dots are experimental; lines are calculated.

So to describe ethylene glycol ethoxylation, we need to consider only two kinetic constants: the initiation constant (k_0) and the propagation constant ($k_p = k_1 = k_2 = \dots$).

The oligomers distribution can be described as a function of the moles of reacted ethylene oxide per mole of starter (EO/S) using the Weibull–Nicander equations,¹³ providing that only two kinetic constants can be considered (k_0 and k_p) and also that the equilibrium proton-transfer constant can be considered independent of the length of the ethoxylated chain ($K_e = K_{01} = \dots = K_{0i} = \dots$). The Weibull–Nicander equations are

$$\text{EO}/S = c \ln \frac{1}{x_0} - (c-1)(1-x_0) \quad (18)$$

$$x_i = \frac{c^{i-1}}{(c-1)^i} \left\{ x_0 - x_0^c \sum_{j=0}^{i-1} \frac{1}{j!} \left[(c-1) \ln \frac{1}{x_0} \right]^j \right\} \quad (19)$$

where

$$c = \frac{k_p}{k_0} K_e \quad (20)$$

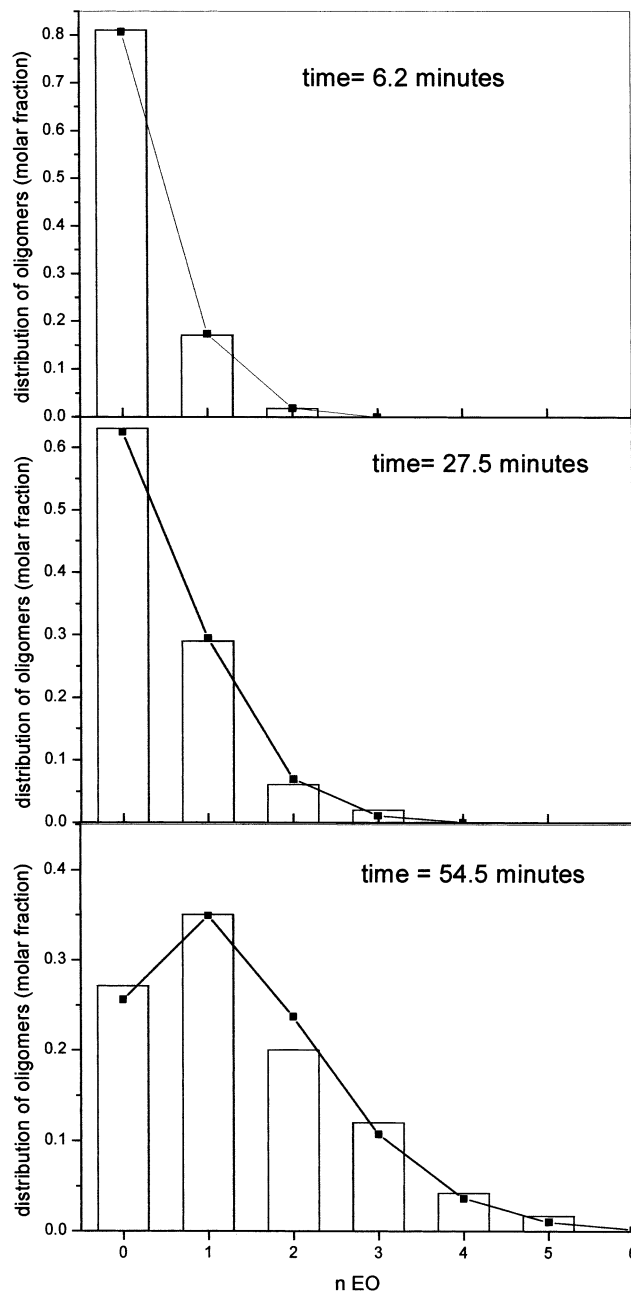


Figure 7. Experimental (bars) and calculated by Flory equation (dots) oligomers distribution related to run A4 of Table 1 at different reaction times.

If the equilibrium proton transfer in eq 17 is independent of the length of the ethoxylated chains, the obtained distributions in the ethoxylation of tetraethylene glycol (runs A4–A6 of Table 1) could be well described by the Weibull–Nicander equations with the parameter $c = 1$ because, in this case, considering tetraethylene glycol as the starter, the initiation constant is equal to the propagation one and K_e should be equal to 1. If $c = 1$, the Weibull–Nicander equations become the simpler Flory equation:¹³

$$x_i = e^{-(\text{EO}/S)} \frac{(\text{EO}/S)^i}{i!} \quad (21)$$

All experimental distributions of runs A4–A6 of Table 1 are well described by the Flory equation, as can be appreciated in Figure 7, where experimental and cal-

culated molar distributions of the oligomers in run A4 are reported as examples. We can conclude, therefore, that K_e is independent of the length of the ethoxylated chains when KOH is used as the catalyst. This finding is in agreement with our previous data.^{17,2,16}

On the basis of the described ethoxylation mechanism and the related kinetic laws (eqs 3 and 15), the following kinetic model can be employed for interpreting all the kinetic ethoxylation runs and simulating the performance of industrial reactors:^{22–24}

$$\frac{d[\text{HOCH}_2\text{CH}_2\text{OH}]}{dt} = -r_0 \quad (22)$$

$$\frac{d[\text{HOCH}_2\text{CH}_2\text{EOH}]}{dt} = r_0 - r_1$$

$$\vdots \quad (23)$$

$$\frac{d[\text{HOCH}_2\text{CH}_2(\text{EO})_i\text{H}]}{dt} = r_{i-1} - r_i$$

$$\frac{d(\text{EO}/S)}{dt} = \frac{V_l}{S} \sum_{i=0,\dots} r_i \quad (24)$$

These equations can be numerically solved provided that the concentrations in the liquid phase of both ethylene oxide ([EO]) and the ionic couples appearing in eqs 13 and 15 are determined before each integration step. Also, the liquid volume (V_l) must be adjusted after each integration step.

The concentration of ionic couples can be calculated using the following equations:

$$[\text{HOCH}_2\text{CH}_2\text{O}^-\text{K}^+] = \frac{[\text{HOCH}_2\text{CH}_2\text{OH}] \cdot C^0}{[\text{HOCH}_2\text{CH}_2\text{OH}] + K_e \sum_{j=1,\dots} [\text{HOCH}_2\text{CH}_2(\text{EO})_j\text{H}]} \quad (25)$$

$$[\text{HOCH}_2\text{CH}_2(\text{EO})_i^-\text{K}^+] = K_e \frac{[\text{HOCH}_2\text{CH}_2(\text{EO})_i\text{H}] \cdot C^0}{[\text{HOCH}_2\text{CH}_2\text{OH}] + K_e \sum_{j=1,\dots} [\text{HOCH}_2\text{CH}_2(\text{EO})_j\text{H}]} \quad i = 1, \dots \quad (26)$$

These equations have been obtained by considering the equilibrium relations (17), together with the mass and charge balances.¹⁷

The kinetic and equilibrium constants of the described model (k_0 , k_p , K_e) have been determined by regression analysis (Buzzi Ferraris, 1968) on the experimental data of runs A1–A6 reported in Table 1, and the obtained values have been reported in the same table. The equilibrium constant has been found to be negligibly dependent on the temperature, as we observed in previous runs performed on alcohol ethoxylation.^{17,16}

The kinetic model and the obtained parameters well describe all the considered kinetic runs A1–A6 of Table 1, as can be seen in Figures 5 and 6, where calculated

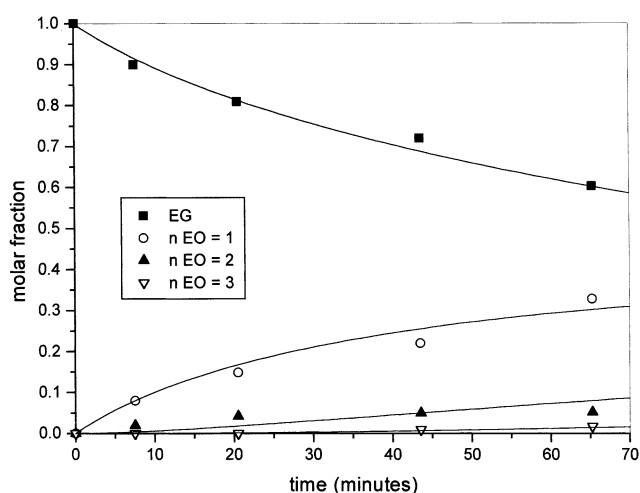


Figure 8. Experimental (dots) and calculated (line) oligomer molar fractions related to run A1 of Table 1 as a function of reaction time.

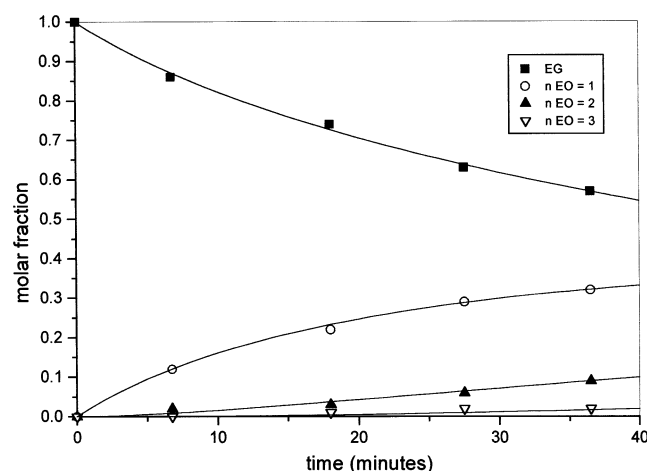


Figure 9. Experimental (dots) and calculated (line) oligomer molar fractions related to A2 of Table 1 as a function of reaction time.

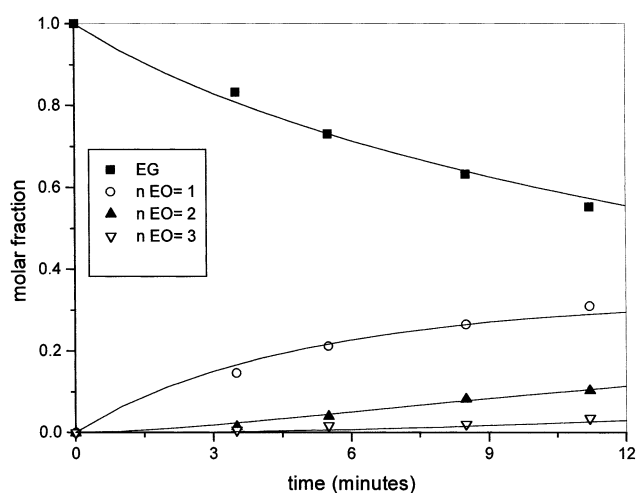


Figure 10. Experimental (dots) and calculated (line) oligomer molar fractions related to A3 of Table 1 as a function of reaction time.

and experimental ethylene oxide consumption rates are reported, and in Figures 8–11, where the agreement of calculated and experimental molar distribution as a function of time for runs A1, A2, A3, and A6 can be observed, as examples.

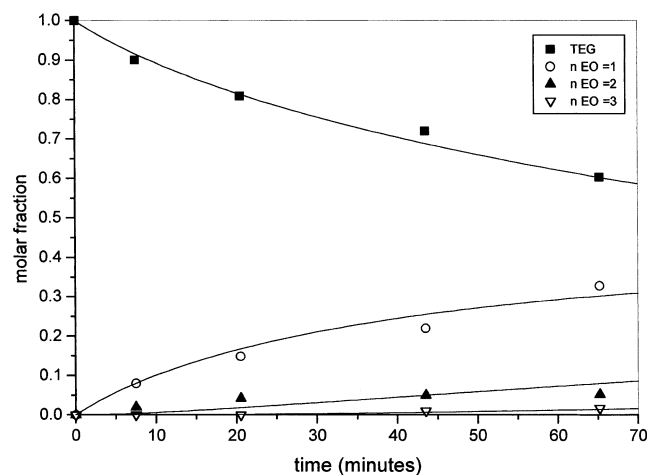


Figure 11. Experimental (dots) and calculated (line) oligomer molar fractions related to A6 of Table 1 as a function of reaction time.

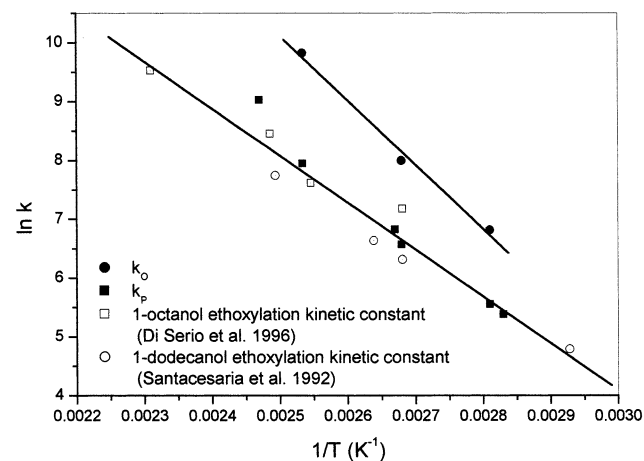


Figure 12. Kinetic constants arranged in an Arrhenius-type plot.

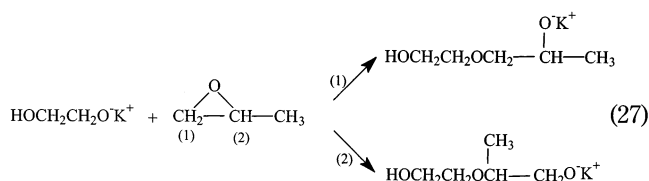
Table 6. Mean Kinetic Parameters for Ethoxylation and Propoxylation

kinetic constants	$\ln A$ ($\text{cm}^3 \text{mol}^{-1} \text{min}^{-1}$)	E (kcal/mol)
k_0	37.5 ± 2.6	21.7 ± 1.9
k_p	28.0 ± 1.4	15.8 ± 1.1
k_{pp}	30.8 ± 1.9	18.6 ± 1.5
k_{ps}	30.3 ± 3.2	19.7 ± 2.5

In Figure 12 the obtained values for k_0 and k_p are reported in an Arrhenius-type plot. As can be seen, k_0 values are higher than k_p ones and the corresponding activation energy is higher, too. In the same figure, the values of k_p , obtained in previous works for the ethoxylation of alcohols,^{17,16} are reported, too. As can be seen, all data are in good agreement and can be interpreted by linear regression for obtaining mean values of pre-exponential factors and activation energies. These values are reported in Table 6. We can conclude, therefore, that the propagation constant is independent of both the length of the ethoxylated chain and the nature of alcohol used as a starter.

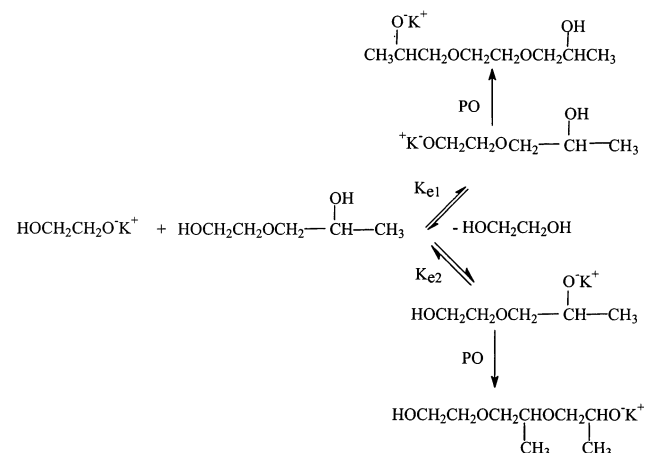
Propoxylation Reaction. Since the mechanism of the reaction is the same for both ethoxylation and propoxylation,¹⁶ also for this reaction we have the in situ formation of the catalyst and the initiation and propagation reactions, but the kinetic scheme is more

complicated. First of all, the asymmetric characteristic of the propylene oxide molecule could generate primary or secondary alcohol when ring opening occurs as a consequence of nucleophilic attack to respectively methylene (1) or methyne group (2). In the case of the initiation reaction we can have, for example:



We can simplify the kinetic scheme considering that contribution of the reaction pathway (2) is negligible in agreement with the literature data.^{16,25} Despite this simplification, the scheme is more complex than that for ethoxylation because the obtained monoadduct is asymmetric, having the possibility to react with the secondary alcoholate group or with the primary alcoholate one, both obtainable by proton-transfer reactions (see Scheme 1).

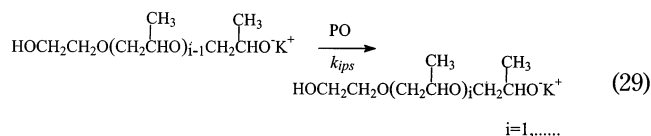
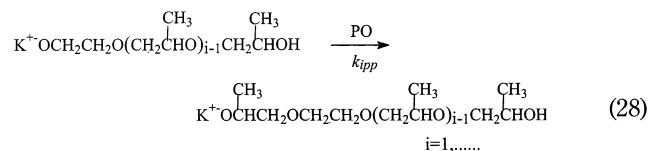
Scheme 1



In the case of reaction with a secondary alcohol group, we obtain the asymmetric biadduct while, when a primary alcohol group reacts, the symmetric biadduct is formed.

Two different adducts can further react, giving more propoxylated species.

In general, for asymmetric adducts we can have two possibilities of reaction involving primary or secondary alcohol groups, such as those in the following scheme.



In the case of symmetric adducts only one type of reaction is possible because only secondary alcohol

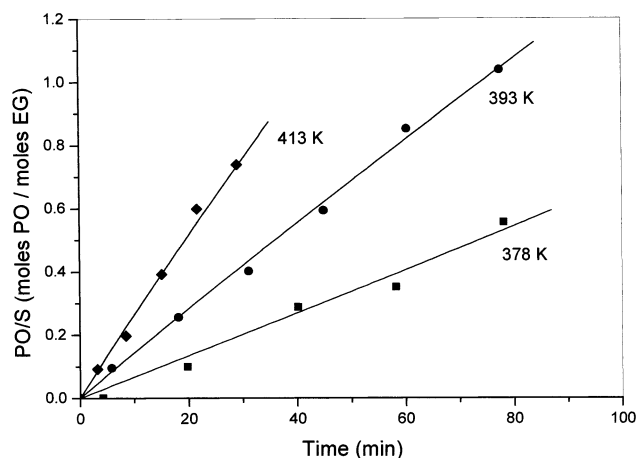
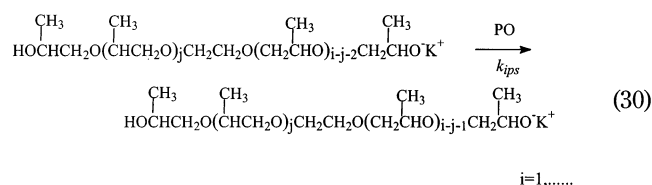
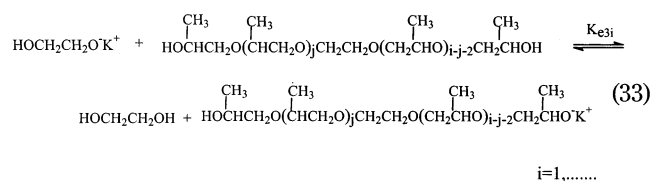
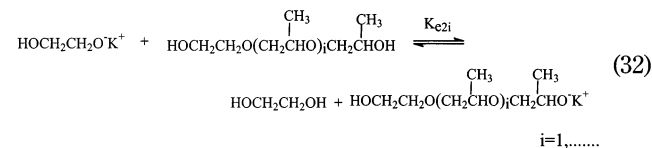
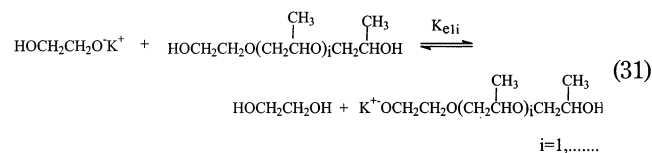


Figure 13. Propylene oxide consumption related to the moles of the starter ethylene glycol (PO/EG) in the propoxylation of ethylene glycol (EG) (runs B1–B3 of Table 2). Dots are experimental; lines are calculated.

groups are present. The occurring reactions are, therefore,



The general proton-transfer reactions are



Propylene oxide consumption, as a function of time, for the runs B1–B3 of Table 2 (ethylene glycol propoxylation) is shown in Figure 13. As can be seen, the rate of reaction is constant with time. By observation of Figures 14–16, it can be noted that the concentration of adduct containing 3 PO is quite low in all cases. This means that the propagation rate on the secondary alcohol is very slow; consequently, for PO consumption only initiation and propagation on the primary hydroxyl of the first adduct are important. We can also conclude that for the runs B1–B3 of Table 2 the initiation and propagation constants for the reaction on hydroxyl groups are about the same, that is, $k_{0p} \approx k_{1p}$.

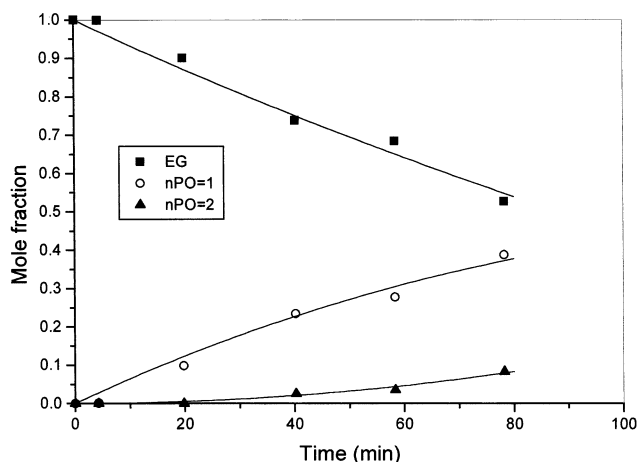


Figure 14. Experimental (dots) and calculated (line) oligomer molar fractions related to run B1 of Table 2 as a function of reaction time.

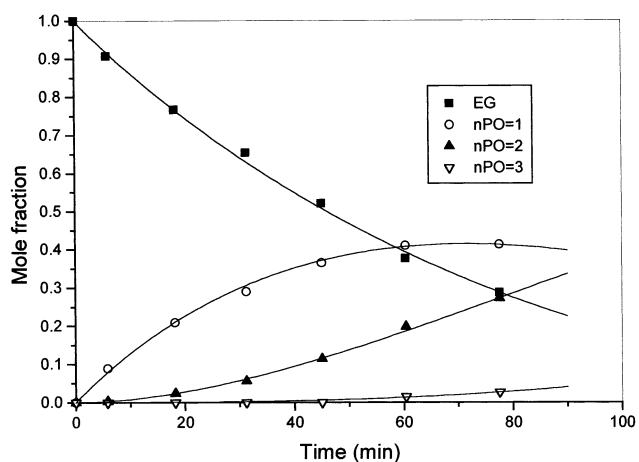


Figure 15. Experimental (dots) and calculated (line) oligomer molar fractions related to B2 of Table 2 as a function of reaction time.

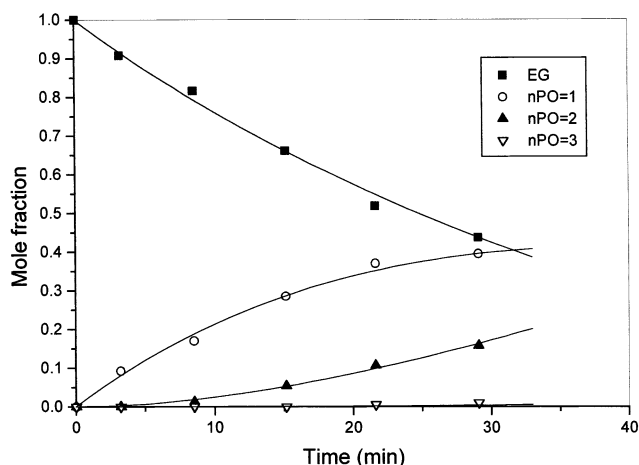
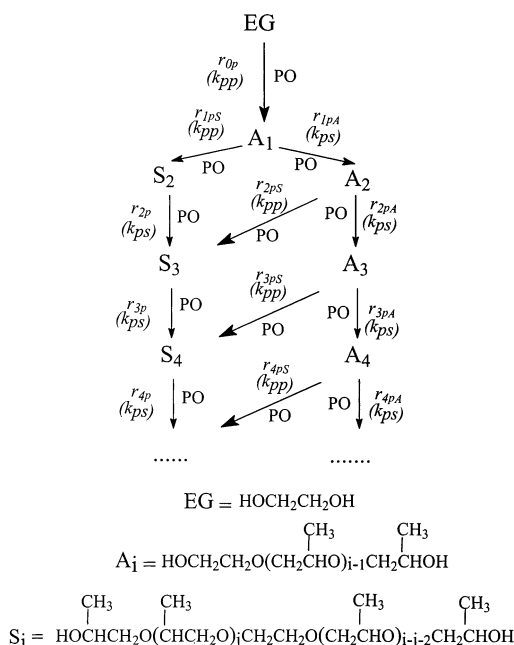


Figure 16. Experimental (dots) and calculated (line) oligomer molar fractions related to B3 of Table 2 as a function of reaction time.

The previous propoxylation kinetic scheme can be simplified by assuming that the propagation constants on primary and secondary alcohol groups are independent of the length of the propoxylated chain, that is, $k_{0p} = k_{1pp} = \dots = k_{ipp} = k_{pp}$ and $k_{1pp} = k_{2ps} = \dots = k_{ips} = k_{ps}$, as reported in Scheme 2.

Scheme 2



On the basis of this scheme, the following kinetic model can be employed for interpreting all the kinetic propoxylation runs of Table 2:

Initiation

$$\frac{d[\text{EG}]}{dt} = -r_{0p} \quad (34)$$

Asymmetric Propagation

$$\frac{d[A_1]}{dt} = r_{0p} - r_{1ps} - r_{1pA}$$

$$\vdots \quad (35)$$

$$\frac{d[A_i]}{dt} = r_{(i-1)pA} - r_{ips} - r_{ipA}$$

Symmetric Propagation

$$\frac{d[S_2]}{dt} = r_{1ps} - r_{2p}$$

$$\frac{d[S_3]}{dt} = r_{2ps} + r_{2p} - r_{3p}$$

$$\vdots \quad (36)$$

$$\frac{d[S_i]}{dt} = r_{(i-1)ps} + r_{(i-1)p} - r_{ip}$$

$$\frac{d(\text{PO}/S)}{dt} = \frac{V_i}{S} [r_{0p} + r_{1ps} + r_{1pA} + \sum_{i=2,\dots} (r_{ip} + r_{ips} + r_{ipA})] \quad (37)$$

The kinetic rates in eqs 34–37 are

$$r_{0p} = k_{pp}[\text{EG}^- \text{K}^+][\text{PO}] \quad (38)$$

$$r_{ip} = k_{ps}[S_i^- \text{K}^+][\text{PO}] \quad (39)$$

$$r_{ips} = k_{pp}[A_{ip}^- \text{K}^+][\text{PO}] \quad (40)$$

$$r_{ipA} = k_{ps}[A_{is}^- \text{K}^+][\text{PO}] \quad (41)$$

where

$$\text{EG}^- \text{K}^+ = \text{HOCH}_2\text{CH}_2\text{O}^- \text{K}^+ \quad (42)$$

$$S_i^- \text{K}^+ = \text{HOCHCH}_2\text{O}(\text{CHCH}_2\text{O})_j\text{CH}_2\text{CH}_2\text{O}(\text{CH}_2\text{CHO})_{i-j-2}\text{CH}_2\text{CHO}^- \text{K}^+ \quad (43)$$

$$A_{ip}^- \text{K}^+ = \text{K}^+ \text{OCH}_2\text{CH}_2\text{O}(\text{CH}_2\text{CHO})_{i-1}\text{CH}_2\text{CHOH} \quad (44)$$

$$A_{is}^- \text{K}^+ = \text{HOCH}_2\text{CH}_2\text{O}(\text{CH}_2\text{CHO})_{i-1}\text{CH}_2\text{CHO}^- \text{K}^+ \quad (45)$$

Considering the equilibrium proton-transfer constant depending only on the type of hydroxyl terminal group,

$$K_{e1} = \frac{[A_{ip}^- \text{K}^+][\text{EG}]}{[\text{EG}^- \text{K}^+][A_i]} \quad i = 1, \dots \quad (46)$$

$$K_{e2} = \frac{[A_{is}^- \text{K}^+][\text{EG}]}{[\text{EG}^- \text{K}^+][A_i]} \quad i = 1, \dots \quad (47)$$

$$K_{e3} = \frac{[S_i^- \text{K}^+][\text{EG}]}{[\text{EG}^- \text{K}^+][A_i]} \quad i = 1, \dots \quad (48)$$

K_{e3} can be assumed equal to $2K_{e2}$ considering that symmetric propoxylated species have two secondary hydroxyl groups.

The concentration of alcoholate species can be calculated from charge and mass balance and result in the following:

$$[\text{EG}^- \text{K}^+] = [\text{EG}] \times \frac{C^0}{[\text{EG}] + (K_{e1} + K_{e2}) \sum_{j=1,\dots} A_j + K_{e3} \sum_{j=2,\dots} S_j} \quad (49)$$

$$[A_{ip}^- \text{K}^+] = K_{e1}[A_i] \times \frac{C^0}{[\text{EG}] + (K_{e1} + K_{e2}) \sum_{j=1,\dots} A_j + K_{e3} \sum_{j=2,\dots} S_j} \quad i = 1, \dots \quad (50)$$

$$[A_{is}^- \text{K}^+] = K_{e2}[A_i] \times \frac{C^0}{[\text{EG}] + (K_{e1} + K_{e2}) \sum_{j=1,\dots} A_j + K_{e3} \sum_{j=2,\dots} S_j} \quad i = 1, \dots \quad (51)$$

$$[S_i^- \text{K}^+] = 2K_{e2}[S_i] \times \frac{C^0}{[\text{EG}] + (K_{e1} + K_{e2}) \sum_{j=1,\dots} A_j + K_{e3} \sum_{j=2,\dots} S_j} \quad i = 1, \dots \quad (52)$$

The kinetic and equilibrium constants of the model described (k_{pp} , k_{ps} , K_{e1} , K_{e2}) have been determined by regression analysis on the data of runs B1–B3 of Table 2, and the values obtained have been reported in the same table. Again equilibrium constants have been found to be negligibly dependent on temperature.

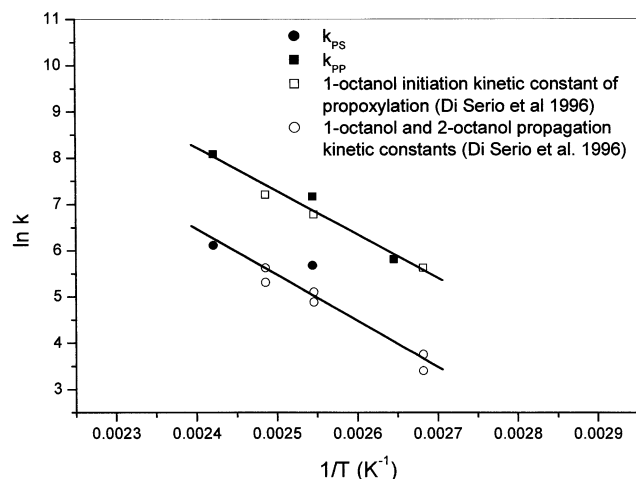


Figure 17. Kinetic constants arranged in an Arrhenius-type plot.

The kinetic model and the obtained parameters well describe all the kinetic runs B1–B3 of Table 2, as can be observed in Figure 13 where the calculated and experimental propylene oxide molar consumption rates are reported, and in Figures 14–16, where the calculated and experimental molar distributions as functions of time for all the runs are reported.

In Figure 17 the k_{pp} and k_{ps} constants are both reported in an Arrhenius-type plot. On the same plots the corresponding constants obtained for the propoxylation of respectively 1-octanol and 2-octanol in a previous paper¹⁶ are reported. As can be seen also in this case the agreement is quite satisfactory and from this plot the mean pre-exponential factors and activation energies for the addition of PO to, respectively, primary and secondary hydroxyl can be determined by linear regression analysis. These values are reported in Table 6.

These results show that also for the propoxylation reaction the kinetic constants are independent of both the chain length and of the nature of alcohol used as the starter.

Conclusions

The kinetics of both ethoxylation and propoxylation of ethylene glycol have been studied by applying two different kinetic models developed on the basis of the occurring reaction mechanisms. These models require very few parameters for describing the evolution with time of alkylene oxide consumption and the corresponding oligomers distributions. In particular, for a given temperature we need two kinetic and one equilibrium constants for the ethoxylation. While for the propoxylation we need two kinetic and two equilibrium constants describing the behavior of both primary and secondary hydroxyl group reactivities.

In the case of ethoxylation we have an initiation constant that is different from the propagation one. The last result is independent of the chain length and is about the same for different types of primary alcohols used as starters.

For the ethylene glycol propoxylation, initiation, and propagation constants, the last related to primary hydroxyls, the results are quite similar and are comparable with the ones obtained for the propoxylation of 1-octanol.¹⁶ The reactivity of secondary hydroxyl groups was much lower than the primary ones. The propagation constant obtained for the reaction with a secondary

hydroxyl is similar to the one found for the propoxylation of 2-octanol.¹⁶ In both cases the propagation constants were, therefore, as for the ethoxylation, independent of the alcohol used as the starter. For these reasons we can drastically reduce the kinetic parameters that are necessary to describe all the kinetic runs.

List of Symbols

- A = pre-exponential factor ($\text{cm}^3 \text{mol}^{-1} \text{min}^{-1}$)
- A_i = acronym for asymmetric propoxylated species
- A_{ip} = acronym for asymmetric primary alcoholate species
- A_{is} = acronym for asymmetric secondary alcoholate species
- A, B, C = constant in correlations (6) and (7) for Wilson interaction parameters
- c = constant in Weibull–Nicander distribution
- C^0 = catalyst total concentration (mol/cm^3)
- d = density (g/cm^3)
- E = activation energy (kcal/mol)
- EG = acronym for ethylene glycol
- k_0 = initiation constant for ethoxylation ($\text{cm}^3 \text{mol}^{-1} \text{min}^{-1}$)
- k_{0p} = initiation constant for propoxylation ($\text{cm}^3 \text{mol}^{-1} \text{min}^{-1}$)
- k_p, k_i = propagation constant for ethoxylation ($\text{cm}^3 \text{mol}^{-1} \text{min}^{-1}$)
- k_{ipp}, k_{pp} = propagation constant for ethoxylation (primary hydroxyls) ($\text{cm}^3 \text{mol}^{-1} \text{min}^{-1}$)
- k_{ips}, k_{ps} = propagation constant for ethoxylation (secondary hydroxyls) ($\text{cm}^3 \text{mol}^{-1} \text{min}^{-1}$)
- K_e, K_{oi} = proton-transfer equilibrium constant for ethoxylation
- K_{e1}, K_{e2}, K_{e3} = proton-transfer equilibrium constant for propoxylation
- $K_{e1i}, K_{e2i}, K_{e3i}$ = proton-transfer equilibrium constant for propoxylation
- n = epoxide adducts number
- M = molecular weight (g/mol)
- P^0 = vapor pressure of epoxides (bar)
- r_0 = reaction rate for ethoxylation (initiation) ($\text{mol}/(\text{min cm}^3)$)
- r_i = reaction rate for ethoxylation (propagation) ($\text{mol}/(\text{min cm}^3)$)
- r_{0p} = reaction rate for propoxylation (initiation) ($\text{mol}/(\text{min cm}^3)$)
- r_{ip} = reaction rate for propoxylation (propagation on secondary hydroxyls) ($\text{mol}/(\text{min cm}^3)$)
- r_{ips} = reaction rate for propoxylation (propagation on primary hydroxyls) ($\text{mol}/(\text{min cm}^3)$)
- r_{ipA} = reaction rate for propoxylation (propagation on secondary hydroxyls) ($\text{mol}/(\text{min cm}^3)$)
- S = moles of substrate (mol)
- S_i = acronym for symmetric propoxylated species
- T = temperature (K)
- TEG = acronym for tetraethylene glycol
- V_l = liquid-phase volume (cm^3)
- x = liquid-phase mole fraction

Subscripts

- AO = generic epoxide (ethylene or propylene oxide)
- EO = ethylene oxide
- PO = propylene oxide
- l = liquid phase
- S = substrate

Greek Letters

- γ = liquid-phase activity coefficient
- Λ = Wilson binary interaction parameters

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